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Effect of ball milling on the production of nanocellulose using mild acid hydrolysis method

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ABSTRACT

Nanocellulose was extracted from two kinds of general cellulose feedstocks, *i.e.*, cellulose paper and cellulose powder, by coupling planetary dry ball milling with mild acid hydrolysis. The effect of ball milling time on the yield and properties of nanocellulose obtained by mild hydrolysis in lower concentration (47 wt%) of sulfuric acid was investigated in details. The obtained nanocellulose was characterized by scanning electron microscopy (*SEM*), Fourier transform infrared spectroscopy (*FTIR*), X-ray diffraction (*XRD*), and thermogravimetric analysis (*TGA*). It is found that the crystallinity and crystal size of ball-milled cellulose decreased with the increase of ball milling time, and the mild acid hydrolysis of the ball-milled cellulose resulted in the crystallinity and thermal stability of nanocellulose at the high temperature range increased but without any changes in chemical structure. It indicates that the appropriate ball-milling of cellulose feedstock could be beneficial for the mild hydrolysis process for the production of high quality nanocellulose with high yield.

1. Introduction

In our daily life, fabrics, ropes, paper and many other consumer goods are made of natural fibers. Most of natural fibers from plants basically consist of cellulose [1], which is the main structure of plant cell wall. Cellulose fiber generally contains two types of structures, *i.e.*, highly ordered (crystalline) and disordered (amorphous) ones [2,3]. Extraction of the crystalline region from microfibrillated cellulose generally results in nanocellulose.

Nanocellulose is considered as a new class of eco-material with many advantages, such as nanoscale dimension, renewability, high surface area, specific high strength and modulus, unique morphology and good optical properties. Thus, it can be used in many fields such as nanocomposite materials, drug delivery, food additive, and filling materials in rubber industry [2,4]. That is why nanocellulose extraction from biomass is an interesting study field nowadays. To date, acid hydrolysis is one of the preferential processes to remove the amorphous regions within the cellulose microfibrils, in which sulfuric acid is the most generally used acid because it produces negative charges on the particles, leading to more stable suspension [3,5].

Many previous studies indicate that the typical concentration of sulfuric acid in hydrolysis reaction for extraction of nanocellulose is near 65 wt% [4]. Dong et al. extracted cellulose microcrystallite from Whatman No.1 filter paper powder (cotton cellulose) using 64 wt% of sulfuric acid with a pulp to acid ratio of 1:8.75 at 45 °C for 1 h [6]. Haafiz et al. isolated cellulose nanowhiskers from microcrystalline cellulose (*MCC*) of oil palm biomass by using 64 wt% sulfuric acid hydrolysis with an acid to MCC ratio of 8.75 mL/g at 40 °C for 1 h [7]. Using lower concentration of sulfuric acid hydrolysis will be more attractive for nanocellulose extraction due to more environmentally friendly and less wastewater from washing step, which will decrease the production cost.

Mechanical process is one of the approaches to diminish cellulosic fibers into nanocelluloses, by which the cellulose size can be reduced by splitting along the longitudinal axis of the cellulose structures via the mechanical stress [3,8]. Planetary ball mill is such a mechanical technique in which the artificial gravity generated by the centrifugal force can be applied to the grinding medium. It is found that the crystallinity of cellulose decreases with the dry ball mill, and as such the nanocellulose could be more easily extracted from the ball-milled cellulose [9–13].

In this study, two general kinds of cellulose, *i.e.*, cellulose paper and cellulose powder, were selected as the raw materials for nanocellulose extraction. To improve the extraction efficiency, the raw materials were pretreated by planetary ball mill at first and then mild hydrolysis of the ball-milled cellulose with lower concentration

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of sulfuric acid at lower reaction temperature for a shorter reaction time was performed. The obtained nanocellulose was characterized by using *SEM*, *FTIR*, *XRD* and *TGA* for investigation of its morphology, the change of chemical composition, crystalline allomorph, crystallinity and crystal size, and thermal stability, respectively. It is expected that such a kind of method can effectively extract nanocellulose from cellulose feedstock.

2. Material and methods

2.1. Materials

Grade 3MM Chr cellulose chromatography paper (Whatman), 38 μm (400 mesh) size of cellulose powder (Wako), and sulfuric acid aqueous solution (47 wt%) were purchased from Wako Pure Chemical Industries Ltd., Japan. The cellulose paper (*CPP*[1]) was crushed by blender for 30 s to small pieces prior to use while the cellulose powder (*CPD*[2]) was used as received.

2.2. Ball milling pretreatment

Cellulose materials were ball-milled with an ITO LP-1 Planetary pot mill. 80 mL of jar with the three different diameters of zirconia ball (10, 5, and 2 mm) was used, in which the ball to material weight ratio (*BMR*) was 12:1 and the weight ratio of the balls with 10, 5, and 2 mm diameters was 5:4:3. In the preliminary experiments, it is found that high rotation speed resulted in very low nanocellulose yield. Thus, in this study, a relative low rotation speed of 300 rpm was selected. The ball milling was carried out for 0.5, 1, 2, and 3 h at room temperature in order to investigate the effect of ball milling time. The pretreated cellulose materials are defined as Ball-milled Cellulose Paper ($BMCPP_x$[3]) or Ball-milled Cellulose Powder ($BMCPD_x$[4]) corresponds to the type of material, while x is the ball milling pretreatment time ($x = 0.5$, 1, 2, or 3 h).

2.3. Acid hydrolysis

Acid hydrolysis was performed by using a low concentration of sulfuric acid aqueous solution (47 wt%). 8.8 mL of acid/1 g of cellulose materials was used in each case. The reaction temperature was controlled at 45 °C with a water bath and the mixing speed was set at 600 rpm The reaction time is fixed at 90 min.

The sulfuric acid hydrolysis was stopped by adding 10-fold cold distilled water (4 °C). The suspension was centrifuged at 8500 rpm for 10 min to get the precipitates and simultaneously remove out the excess acid. The precipitate was then suspended in distilled water, followed by centrifugation. This process was repeated until the neutral pH was achieved. Subsequently, the suspension was frozen in freezer at −30 °C, then dried in freeze-dryer. The dried product was stored in vacuum for further characterizations. The obtained products are defined as Nanocellulose from cellulose materials; Nanocellulose from cellulose paper (*NCCPP*[5]), Nanocellulose from cellulose powder (*NCCPD*[6]), Nanocellulose from ball-milled cellulose paper at x h of ball milling pretreatment time ($NCBMCPP_x$[7]), and Nanocellulose from ball-milled cellulose powder at x h of ball milling pretreatment time ($NCBMCPD_x$[8]).

[1] *CPP*: cellulose paper.
[2] *CPD*: cellulose powder.
[3] $BMCPP_x$: ball-milled cellulose paper at x h of ball milling time.
[4] $BMCPD_x$: ball-milled cellulose powder at x h of ball milling time.
[5] *NCCPP*: nanocellulose from cellulose paper without ball milling pretreatment.
[6] *NCCPD*: nanocellulose from cellulose powder without ball milling pretreatment.
[7] $NCBMCPP_x$: nanocellulose from ball-milled cellulose paper at x h of ball milling time.
[8] $NCBMCPD_x$: nanocellulose from ball-milled cellulose powder at x h of ball milling time.

2.4. Characterization

Surface morphologies of samples were examined by a scanning electron microscope (*SEM*, SU8010, Hitachi) at an acceleration voltage of 1.0 kV. A drop of diluted product suspension was deposited on the carbon tape and air-dried at 50 °C oven for 2 h. Then, the sample was sputter-coated with Pt at 15 mA for 20 s to avoid charging.

Fourier transform infrared spectroscopy (*FT-IR*) was recorded by using Jasco *FT/IR*-4200 infrared spectrophotometer with wavelengths in the range of 500–4000 cm^{-1}, in which the sample was ground into fine powder and mixed with KBr followed by pressing the mixture into thin pellet.

To study the crystallinity, X-ray diffraction (*XRD*) was carried out on a Rigaku Smartlab X-ray diffractometer with *Cu Kα* radiation at 45 kV and 200 mA from 10–50° (2θ angle range). The crystallinity was calculated using peak height method. It is calculated from the height ratio between the intensity of the crystalline peak and the total intensity after the subtraction of the background signal (non-crystalline) according to the following equation:

$$C\ (\%) = 100 \times \frac{I_{200} - I_{non-cr}}{I_{200}} \quad (1)$$

where C is the apparent crystallinity [%], I_{200} is the maximum intensity of the peak corresponding to the plane in the sample with the Miller indices 200 at a 2θ angle between 22–24° and $I_{non\text{-}cr}$ represents the intensity of diffraction of the non-crystalline material, which is taken at an angle of about 18° (2θ) in the valley between the peaks [14].

The Scherrer equation was used to calculate the crystallite size, t (nm), which is determined perpendicular to the (200) planes for both cellulose I and cellulose II samples:

$$t = \frac{0.9\lambda}{\beta \cos\theta} \quad (2)$$

where λ is the radiation wavelength for Cu, θ is the diffraction angle, and β is the corrected angular width at half maximum intensity in radians [15].

The thermal stability of sample was determined by using a thermogravimetric analyzer (DTG-60H, Shimadzu). An average mass of 10 mg of the sample was put in an alumina cup and heated from room temperature to 600 °C at a heating rate of 10 °C/min under a nitrogen flow of 50 cm^3/min. Differential thermal gravimetry (*DTG*) was calculated based on *TGA* values using a forward finite difference method as the following equation:

$$\mathrm{DTG} = \frac{(W_{t+\Delta t} - W_t)}{\Delta t} \quad (3)$$

where $w_{t+\Delta t}$ and w_t are the residual weight of sample at time $t+\Delta t$ and t, respectively, and Δt is the time interval for reading residual sample weight [16].

3. Results and discussion

3.1. Product yield

The weight of final product was recorded and calculated as product yield based on 100% of raw cellulose or ball-milled cellulose materials for acid hydrolysis. The yields of all final products were tabulated and shown in Table 1. The average yield of nanocellulose from *CPP* and $BMCPP_x$ was 85.1%, while the average yield of nanocellulose from *CPD* and $BMCPD_x$ was 83.7%. It is found that these obtained nanocelluloses yields are higher than those reported in other previous work with similar condition. Bondeson et al. isolated nanocellulose from microcrystalline cellulose by hydrolysis in 63.5 wt% sulfuric acid at 45 °C for 2 h. The yield of their obtained product was only 30% [17]. As such, mild acid hydrolysis of ball-milled cellulose can extract