Preparation and Characterization of Pineapple Leaf Nanocellulose by High Pressure Homogenization

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Abstract. Nanocellulose was extracted from pineapple leaf using high pressure homogenization (HPH) in a liquid, homogeneous state. After optimizing conditions, nanocellulose was obtained at 100 MPa for 45 cycles with the diameter of 4-10 nm. The nanocellulose was cellulose II, with the crystallization index reducing from 69.68% to 34.25%. The specific surface area of nanocellulose, Water-Holding Capacity and Oil-Holding Capacity were increased after high pressure homogeneous treatment. The new process can effectively open up a new direction for high-added-value applications of pineapple leaf.

Introduction

Pineapple leaf is a waste product of pineapple cultivation, which is found to be multicellular and lignocellulosic. The efficient utilization of this biomass for functional materials has attracted more attention around the world because of its high cellulose content with renewable characteristics. Recently, nanocellulose was used in material [1], electrical [2], medicine [3], chemical [4], food [5] and even superconductivity, due to its superior properties, such as high strength, low specific heat coefficient, large specific surface area, good water-holding capacity and good oil-holding capacity etc. In previous studies, nanocellulose was prepared through ball-milling process [6] and hydrolysis method [7,8]. However, there is still a big technical problem in industrial production: for example, mechanical method has the shortcoming of high energy consumption and low production efficiency [9]. Preparation of nanocellulose by hydrolysis method is low efficiency and caused serious pollution to the environment. Therefore, how to produce nanocellulose effectively, is still a problem to be resolved.

In this study, cellulose separation and refinement in liquid phase conditions, can reduce the cellulose chain between each other "sliding" resistance, and to exert certain physical force, make the fiber in a liquid, homogeneous state complete network structure collapse and the molecular chain of self-assembly [10,11]. pineapple leaf nanocellulose was prepared by cellulose liquid homogeneous nanometer technology, and was then characterized in physical and chemical properties, such as the particle size distribution in the water phase, specific surface area and porosity, swelling property, water-holding capacity, oil-holding capacity, etc. In order to later provides the theory basis for pineapple leaf fiber products nanotechnology applications.

Experimental

Materials and Methods

Pineapple leaf was obtained from zhanjiang plantations, collected by agricultural machinery research institute, Chinese academy of tropical agricultural sciences, China. The ionic liquid of 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) used in this study was synthesized in our previous

study. All chemical reagents were of analytical grade, and purchased from Guangzhou Chemical Reagent Factory (Guangzhou, China).

Pretreatment of pineapple leaf and dissolution of cellulose: the original pineapple leaf was pretreated with sodium hydroxyl solution of 35 g/L for 6 h at 95°C to remove the impurities.the cellulose was obtained with the ratio above 83.13 wt%.Then certain cellulose (3wt%) was dissolved in the synthesized ionic liquid at 150 °C by microwave heating with 400W[11].

Preparation of nanocellulose by high pressure homogenizer: the cellulose/BmimCl solution was then passed through a high pressure homogenizer with a certain cycles at a certain pressure. Then five times as much as quality of boiled deionized water was added into the homogeneous solution, and stirred for 10 min on the magnetic stirrer to make the nanocellulose precipitation from homogeneous system. Afterwards repeatedly centrifugal washing, the supernatant fluid was clarificated by high-speed refrigerated centrifuge. Finally, the regenerated nanocellulose was dried in the vacuum freeze drier until reaching a constant weight[10].

Analysis

The structure properties of cellulose extracted from pineapple leaf before and after homogeneous isolation were characterized by transmission electron microscopy (TEM), infrared spectroscopy (FT IR), X-ray diffraction (XRD), thermo gravimetric analysis (TGA), and etc.

Transmission Electron Microscopy (TEM) Analysis

The morphology measurements of the pineapple leaf nanocellulose were characterized by transmission electron microscopy (TEM) (JEM-100, JEOL, Tokyo, Japan) operated at 100 keV.

Infrared Spectroscopy (FT IR) Analysis

Using KBr tabletting method to measure the infrared spectrum by the fourier transform infrared spectrometer (Spectrum GX-1, PerkinElmer, USA) in the range from 4000 to 400 cm^{-1} .

X-ray Diffraction (XRD) Analysis

The crystal structure of the sample after homogeneous isolation was measured by X-ray Diffractometer (Rint-Ultima+, Rigaku, Japan). Technical parameters: Cu (K α wavelength λ =0.154nm) radiation at 40 kV and 20 mA, at a speed of 0.04°s-1 in the range 20-80°.

Thermo Gravimetric Analysis (TGA)

The thermo gravimetric curve was tested by thermo gravimetric analyzer (STA449C/4/G, Netzsch, Germany). Technical parameters: the static TGA mode, temperature range $25 \sim 800^{\circ}$ C, selects the N₂ protection, heating rate 10° C /min.

The Properties of Nanocellulose

Particle Size Measurements

Particle sizes of nanocellulose under the condition of different homogeneous isolation were determined by the Nano-ZS (Malvern Instruments,UK), as the refractive index is 1.50, the temperature is 25 °C. A little pineapple leaf nanocellulose was put into a beaker, then diluted in 100 ml deionized water with ultrasound for 3 min to make the solution dispersed evenly.

The Specific Surface Area and Porosity

The specific surface area and porosity of the samples were measured using the Brunauer–Emmett–Teller (BET) with five-point method under 77K in N_2 atmosphere (Surface area and porosity analyzer, ASAP2020-M,Micromeritics, USA).

The Swelling Capacity

1.0000g sample was immersed into a graduated cylinder at 25 °C to observe the swelling behavior. After 24h, the expansion volume was measured until there was no further change in the volume. The degree of swelling ratio was measured by the following Eq.1[12]:

$$\mathbf{S} = \frac{V_2 - V_1}{m} \tag{1}$$

Where S is swelling capacity, V_2 , V_1 are the volume of solution with and without sample, respectively. m is the weight of sample.

The Water-Holding Capacity

1.0000g of sample was stirred in 10 ml of deionized water for 24 h in a 50 ml centrifuge tube at room temperature. After samples were centrifuged (4000g, 30 min), the supernatant was transferred to a graduated cylinder of 10mL, where the volume was measured. Water-Holding Capacity was calculated as 10 ml minus the volume of water in graduated cylinder[13].

The Oil-Holding Capacity

1.0000g of sample was stirred in 10 ml of corn oil for 24 h in a 50 ml centrifuge tube at room temperature. After samples were centrifuged (4000g, 30 min), the supernatant was transferred to a graduated cylinder of 10mL, where the volume was measured., Oil-Holding Capacity was calculated as 10 ml minus the volume of corn oil in graduated cylinder[13].

Results and Discussion

Effects of HPH Pretreatment on Particle Sizes

3% (w/w) pineapple leaf cellulose/BmimCl solution was passed through the high pressure homogenizer under 80 MPa with different cycles at room temperature[14]. Fig. 1a shows the effects of different homogeneous cycles on particle size of pineapple leaf nanocellulose. With the increase of homogeneous cycles, the particle size of nanocellulose was decreased until 45 cycles and then increased again. It suggested that the network of pineapple leaf cellulose was broken with the increasing homogeneous cycles at first. But when the particle sizes reduced to a certain extent, the intermolecular attraction became stronger, and there were much stronger reunion between particles to obtain bigger particle sizes.





Fig. 1. Effects of homogeneous treatment on the particle size (a: Cycles; b: Pressure).

Effects of different homogeneous pressure on particle sizes are shown in Fig.1.b. The particle size of nanocellulose decreased with the increased homogeneous pressure until 100MPa, and then increased. It was due to the interaction of shearing force, collision force and cavitation interaction among the pineapple leaf cellulose. The molecular chain of nanocellulose was interrupted seriously and the particle size of nanocellulose decreased with the homogeneous pressure increased. But as the processing pressure continued to increase, the particle size of nanocellulose was prone to reunite by the van der Waals force, leading to the increased particle size.

Hence, the optimal homogeneous conditions were as follows: 3% (w/w) pineapple leaf cellulose/BmimCl solution was through the high pressure homogenizer under an operating pressure of 100 MPa with 45 cycles at room temperature.

Structure Analysis of Nanocellulose by TEM, FT-IR, XRD, TGA



Fig. 2. TEM micrographs of nanocellulose.

The structure of pineapple leaf cellulose was destroyed during the process and the formed nanocellulose particles. After treatment under the optimal conditions, nanocellulose particles presented regular spherical shapes and good dispersion, with 4-10 diameter size shown in Fig. 2.

Infrared Spectrum Analysis



Fig. 3. FT-IR spectra of regenerated cellulose (a), nanocellulose (b).

Fig. 3 shows FT-IR spectra of regenerated cellulose (a), nanocellulose (b). The two spectra were very similar, which was demonstated that high pressure homogeneous process did not change the main structure of the pineapple leaf cellulose. The O-H vibration peak of nanocellulose was moved from to 3412 cm⁻¹ to 3418 cm⁻¹ during the process. It indicated that intermolecular and intramolecular hydrogen bonding between the cellulose molecular chains was receded.

Specially, the peak at 1429 cm⁻¹ (CH2 scissor movement) was broaden after HPH, which was suggested the intramolecular hydrogen bonding of pineapple leaf cellulose (hydrogen bonding at C6) were destroyed during HPH pretreatment.

Crystal Structure Analysis (XRD)



Fig. 4. XRD patterns of nanocellulose.

Fig. 4 shows the crystal structure of nanocellulose after HPH. It can be seen that nanocellulose has strong diffraction peak in 11.7 $^{\circ}$, 20.3 $^{\circ}$ and 21.7 $^{\circ}$, which belonged to cellulose II structure [15,16].

Consistent with FT-IR results, high pressure homogeneous process is a physical process, and there is no obvious change in the structure of cellulose. However, the crystallinity was reduced from 69.68% to 34.25% after HPH treatment. This was due to intermolecular and intramolecular hydrogen bondings of the cellulose were attacked, and the ordered crystalline region changed to amorphous region, leading to the declined crystallinity dramatically [17].

Thermo Gravimetric Analysis (TGA)

The thermo gravimetric analysis of regenerated cellulose and nanocellulose are shown in Table 1. The initial decomposition temperature and the termination decomposition temperature of pineapple leaf nanocellulose were down to 310.9 °C and 345.4 °C respectively. It suggested that the thermal stability decreased during HPH process, which was due to the damages in crystal region between cellulose.

sample	initial temperature /°C	Maximum decomposition rate/°C	termination temperature/°C
Regenerated cellulose	312.6	340.6	354.2
Nanocellulose	310.9	338.6	345.4

Table 1. The different temperature of regenerated cellulose (a) and nanocellulose (b).

The Properties of Nanocellulose

Table 2.	The physical	properties	of regenerated	cellulose and	nanocellulose.
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Item	regenerated cellulose	nanocellulose
Specific surface area m^2/g	2.0	2.8
porosity cm ³ /g	2.5	2.1
swelling capacity ml/g	4.0	1.7
Water-Holding Capacity g/g	4.9	5.4
Oil-Holding Capacity ml/g	5.6	5.8

Table 2 presents the physical properties of regenerated cellulose and nanocellulose. It shows that the specific surface area increased and the porosity decreased after HPH. This was due to the cellulose reticular structure was destroyed in the process, with the large gap of mesh structure into a spherical particle, leading to increased the specific surface area and decreased the porosity [18].

Swelling capacity is a specific technical index for cellulose. Through the calculation of Eq.1, the swelling capacity of nanocellulose was down to 1.7 ml/g after HPH. This was because the reticular structure of cellulose was destroyed from big mesh structure into round spherical particles. Therefore, reduced moisture was passed into the interior of the cellulose channels, thus affecting the swelling capacity of cellulose.

The water-holding capacity (whc) and oil-holding capacity (ohc) are reflecting the ability to absorb and retain water /oil of pineapple leaf cellulose. Table 2 shows the whc and ohc of nanocellulose were higher than regenerated cellulose. It was mainly because the specific surface area of cellulose increased and surface active was strengthened and enlarged the contact area with water molecules and grease molecules. Nanocellulose because of its good whc and ohc, so in make up cotton, nano mask has had the very big development, the partial products have industrialization, at the same time it also has application in cosmetics ingredients.

Summary

In this study, the pineapple leaf nanocellulose was prepared by high pressure homogenization in ionic liquids. The effects of preparation process on particle sizes and structure were studied, and the optimal homogeneous conditions were 3% (w/w) pineapple leaf cellulose/BmimCl solution through the high pressure homogenizer under an operating pressure 100 MPa with 45 cycles at room temperature. The change of structure performance and the properties of pineapple leaf cellulose before and after HPH treatment was characterized. The results showed that nanocellulose particles are spherical and reunion with the diameter of 4-10 nm, and the crystal structure of nanocellulose belonged to cellulose II, but the crystallinity, thermal ability, porosity and swelling capacity were reduced. The specific surface area, water-holding capacity and oil-holding capacity of nanocellulose were increased after HPH, which can be used for coating, film, textiles, cosmetics, food, composite materials, etc.

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