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# Fabrication and characteristics of cellulose nanofibril films from coconut palm petiole prepared by different mechanical processing

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ABSTRACT

This paper focused on extraction of cellulose nanofibrils (CNFs) from coconut (*Cocos nucifera* L.) palm petioles falling off naturally, which if not properly processed constitute an environmental hazard. CNFs were isolated by chemical pretreatments and different mechanical processing, including grinding (G), grinding followed by ultrasonication (GU), and grinding followed by homogenization (GH). As one of the applications of this biodegradable and renewable CNFs, fabrication of films without using an organic solvent has been attempted using the received CNFs. Fourier transform infrared spectroscopy (FTIR) spectra analysis showed that the chemical treatment removed most of hemicellulose and lignin from the palm petioles, remaining only cellulose. SEM observations showed that diameter of the CNFs from GU method was between 50 and 100 nm, and the aspect ratio of CNFs was over 1000. Tensile properties and transmittance of CNFs films with different mechanical treatments were also studied. Compared to grinding treatment, the CNFs film prepared by grinding/ultrasonication and grinding/homogenization treatments presented better tensile properties and transmittance. This work provides a new approach for more effective utilization of coconut palm petiole as potential feedstock for CNFs.



## 1. Introduction

With the decline of natural resources and the rising cost of raw fiber materials, the use of non-traditional sources such as forest and agricultural residues as raw materials has become more and more necessary for industry (Xing et al., 2006, 2007). The renewable, low-cost, lightweight and high specific strength, and stiffness have identified these natural fibers as ideal reinforcement materials for polymer composites (Wu et al., 2010). Coconut palm (*Cocos nucifera* L.) is spread widely in tropical and sub-tropical regions as an important plant for local economy. The nutritious nut provides large amounts of food for people, but at the same time, million tons of residues cause serious solid waste pollution and air pollution because of they are either dispersed in fields and cities without rotting, or burnt. With the increasing attention on sustainable and environmental friendly materials, there are more and more studies about using natural fibers as reinforcement in polymer-matrix composites (Bledzki et al., 2010; Agunsoye et al., 2012). In order to explore new approaches for more effective utilization of coconut agricultural residues, Maheswari et al. (2012) extracted cellulose microfibrils with diameters in the range of 10–15 μm from the agricultural residue of coconut palm leaf sheath using chlorination and alkaline extraction process method. Rosa et al. (2010) also prepared cellulose nanowhiskers from coconut husk fibers under different preparation conditions. However, there are very few reports in the literature about the extraction and applications of cellulose micro and/or nanofibrils from coconut palm petiole residues.

In recent years, a particular natural fiber derivative, CNFs have received major attention for its superior mechanical properties and have been used as promising candidates for reinforcement materials in nanocomposites (Abe and Yano, 2009; Bras et al., 2010; Chirayil et al., 2014). Cellulose is an abundant and naturally occurring polymer that mainly comes from wood and agricultural plants. Much effort has been made to develop adequate and commercially viable processes for disintegrating cellulose fibers into their structural components at nanoscale (Fan et al., 2009). Grinding, high-pressure homogenization, high-intensity ultrasonication, and enzymatic methods have been the principal applied procedures for the fibrillation of plant fibers. Iwamoto et al. (2005) prepared CNFs

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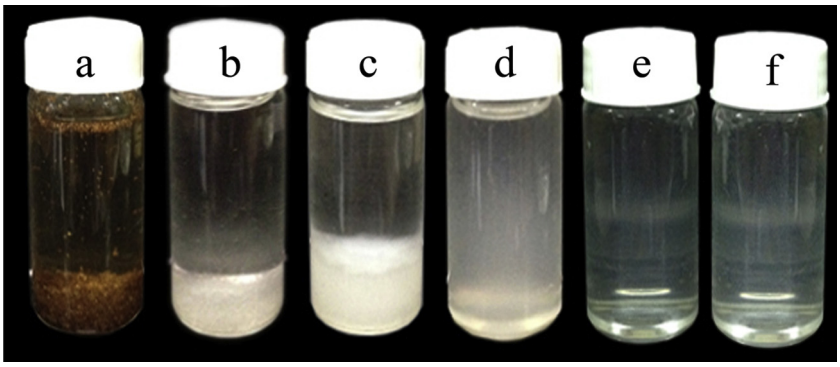


**Fig. 1.** Photographs of the samples in different stages: (a) dewaxing, (b) bleaching, (c) alkali-treatment, (d) G, (e) GU, and (f) GH.

from pulp fiber by a high-pressure homogenizer treatment and a grinder treatment, and found that the grinder treatment resulted in the successful fibrillation of wood pulp fibers into nanofibers. Li et al. (2012) isolated CNFs with 10–20 nm in diameter from sugarcane bagasse by high-pressure homogenization in an ionic liquid (1-butyl-3-methylimidazolium chloride). Zhao et al. (2013) also extracted cellulose nanofibrils with diameters mainly ranged from 16 to 28 nm from dry softwood pulp through high shear homogenization. Chen et al. (2011a,b) individualized cellulose nanofibers ranged from 5 to 20 nm from poplar wood using high-intensity ultrasonication combined with chemical pretreatments, and found that the diameter distributions of the resulting nanofibers were highly dependent on the output power of the ultrasonic treatment. From the literature, it is difficult to identify the most appropriate treatment method for producing CNFs among the grinding, homogenization, and ultrasonication methods.

In cell walls, cellulose microfibril bundles exist encased by the embedding matrix such as hemicellulose and lignin, and the removal of such matrix substances is necessary for the fibrillation process. In this paper, chemical pretreatments were used at first to remove most of wax, extractives, hemicelluloses, and lignin of coconut palm petioles, and then different mechanical treatments, including grinding, grinding followed by ultrasonication and grinding followed by homogenization were introduced to disintegrate cellulose fibers into nano scale fibrils. There is also an urgent need for local government in south China to deal with the large amount of palm petioles wastes. Therefore, the objective of this paper was to convert the unfriendly falling off coconut palm petioles residues into biodegradable and renewable value-added products CNFs, and to explore the feasibility of fabricating CNFs films without organic solvents. The structure and properties of prepared CNFs films were characterized by tensile test, scanning transmission electron microscopy (STEM), Fourier transform infrared (FTIR) analysis, and optical performance test.

## 2. Experimental details

### 2.1. Materials

Woody powder from coconut palm petioles (coming from Hainan province, China), cleaned with water and air dried, broken to the size of 2–3 mm × 6–7 mm with a L-905 shredder, grinded into powders with a FZ102 miniature plants grinder (TAISITE instrument Co., Tianjin), and sieved under 100 mesh (Zhang Xing Sand Screen Factory, Zhejiang province), was used for this study. The chemical composition of the coconut palm petioles was preliminarily investigated, and the content of cellulose, hemicelluose, lignin, and ash were 33.29 wt%, 33.61 wt%, 19.87 wt%, and 5.5 wt% (on a dry weight basis), respectively (Zhu et al., 2014). Chemical agents, including benzene, ethanol, sodium chlorite, hydrogen peroxide, and potassium hydroxide were purchased from Nanjing Chemical Reagent Co., Ltd.

### 2.2. Preparation of CNFs

Firstly, coconut palm petiole powder (10 g) was dewaxed with 2:1 (v/v) mixture of benzene/ethanol for 6 h in a Soxhlet apparatus (SXT-06, Shanghai Hongji Instrument Co., Ltd.). The main purpose of this step is to remove off waxes and extractives according to open literatures (Abe and Yano, 2009; Chen et al., 2011a,b; Pettersen, 1984). Secondly, the dewaxed powder, as shown in Fig. 1a, was bleached using 1 wt% acidified sodium chlorite water solution (400 mL) at 75 °C for an hour, and the process was repeated for four times, resulting in a white mixture, and then the mixture was washed with distilled water until the residue was neutral (shown in Fig. 1b). This step mainly removed off the lignin in the fibers according to Abe and Yano (2009). Thirdly, in order to purify the cellulose by removing hemicellulose, residual starch and pectin, the bleached sample was further treated using 6 wt% potassium hydroxide water solution (400 mL) at 90 °C for 2 h, and then filtered and rinsed with distilled water until the residues were neutralized, as shown in Fig. 1c. Finally, the slurry of 1 wt% purified cellulose in water was processed by grinding (G), grinding followed by ultrasonication (GU), and grinding followed by homogenization (GH) treatment, respectively, resulting in cellulose suspension. Grinding process was done for 15 times with a MKCA6-3 grinder (Masuko Corp., Japan) at 1500 rpm. Ultrasonication process of the ground cellulose was conducted in an ice/water bath for 40 min at 20–25 kHz frequency with an output power of 960 W by an ultrasonic generator (XO-1200, Xianqu Biological Technology Co., Ltd., China) with a cylindrical titanium alloy probe tip (2.5 cm in diameter). A 250 mL glass beaker with 5 cm in diameter and 10.8 cm in height was used as the recipient. At the same time the ground cellulose was subsequently processed twice with a homogenizer (EmulsiFlex-C3, AVESTIN, Inc., Canada) at pressure of 105 kPa.

### 2.3. Fabrication of CNF films

CNF films were fabricated according to the method by Iwamoto et al. (2005). The obtained cellulose nanofibers were dispersed in water at a fiber content of 0.1 wt% with stirring for 24 h with a magnetic agitator. Fig. 1d–f was the water suspensions of cellulose nanofibrils obtained by gringing (G), grinding/ultrasonic (GU), and grinding/homogenizing (GH), respectively. A 500 mL water suspension was vacuum filtered using a polytetrafluoroethylene membrane filter with a mesh of 0.2 μm and a diameter of 40 mm, resulting in a thin mat. The mat was then sandwiched between two water cellulose filter membranes, which were loaded between two smooth glass plates, and dried at 60 °C for 48 h in an oven (DZF-6090, Jinghong Laboratory Equipment Co., Ltd., China). Three types