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EASY CELLULOSE NANOFIBER EXTRACTION FROM RESIDUE OF AGRICULTURAL CROPS

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Cellulose is found in the cell wall of plant fibers in the form of nanofibers. The Young's modulus of the crystalline portion is close to 140 GPa whereas the tensile strength of nanofibers is estimated to be above 2 GPa. Cellulose nanofiber has the potential to become an environmentally benign substitute for conventional reinforcements, but the overall cost of production is prohibitive due to the high energy demand and low yields of the mainstream processes, along the need of expensive devices for proper extraction. This study proposes the use of an affordable kitchen blender adapted to extract cellulose nanofiber from agricultural crop byproducts to reduce production cost. Preliminary results showed that blending of pulp fibers from grass straw produces nanofibers similar to commercially available morphologies. So far the raw material for nanofiber extraction has been mainly pulp fibers from wood, but the availability of cellulose in plant cells other than fibers would make nanofibers accessible to a wider research community and accelerate the development of cellulose-based nanocomposites.

Keywords: Cellulose; nanofiber; plant cell; agricultural crop.

1. Introduction

Cellulose is the most abundant polysaccharide available in nature and is photosynthesized from carbon dioxide and water using solar energy. Most of the cellulose is found in the cell wall of plant cells, in which the smallest element is known as nanofibers. These tiny fibrils have a diameter of a few tens of nanometers, and are made up of a bundle of long cellulose molecular chains arranged in a semi-crystalline structure. The tensile modulus and strength are comparable to those of aramid fibers [1]. Cellulose nanofibers can be used as reinforcement in composites and when combined with a bioplastic, produce completely environmentally friendly materials. Besides, cellulosic fibers have the ability to mutually interact by hydrogen bonds in well dispersed systems forming a percolated system, increasing the reinforcing effect in composites over systems in which the stress transfer occurs only between matrix and reinforcing phase [3, 4].

In general cellulose nanofibers have been extracted from wood, but non-wood plants like those of the Gramineae family (grass, cereals, reed, bamboo) are also potential sources. Extraction of nanofibers is mostly based on mechanical nanofibrillation processes but still relying on expensive devices, with high energy demand but low production yields. A more affordable mechanical process to extract cellulose nanofibers using a kitchen blender was demonstrated by Uetani et al. [5]. We propose the modification of the design of a kitchen blender bottle to optimize the fibrillation of fibers, by implementing some features lacking in the original bottle intended to process food. The design aims to increase the probability of fibers colliding against the blades and breaking the cell wall of the fibers, ultimately promoting nanofibrillation.

2. Experimental

2.1. *Chemical pre-treatments for pulping*

The raw materials for the extraction of nanofibers consisted of grass (gramineous weed), sweet potato vine, and Japanese citrus fruit locally known as "sudachi" (*Citrus sudachi*) residue after juice extraction. Initially, 30 g of grass or sweet potato vine was mixed with water and blended for 20 to 30 seconds in order to chop them into shorter bundles about 3 mm long. Next, a mixture of 1 L of distilled water, 10 g of sodium chlorite, and 2 mL of acetic acid was prepared, in which the grass or vine was immersed and stirred at 70°C. The same amounts of sodium chlorite and acetic acid were added to the mixture every 1 hour of treatment, totalizing 3 hours of treatment to completely remove lignin. After rinsing the fibers with water, they were dipped in 1 L of aqueous solution containing 6 wt% potassium hydroxide at 80°C, and stirred for 3 hours. After each treatment, fibers were washed by running water until pH became neutral, resulting in wet pulp fibers. The same treatment was conducted on sudachi residue with the only exception of the initial amount consisting of 200 g, due to a much lower final pulp fiber yield compared to grass and sweet potato vine.

2.2. *Fibrillation of pulp fibers into nanofibers*

Mechanical fibrillation was performed by a household blender Vitamix TNC 5200 (Vitamix Corporation, USA), with a modified bottle. Pulps of grass, sweet potato vine, and sudachi residue made into aqueous suspensions of 1 wt% fiber content were blended at 37,000 rpm for ten minutes at reduced pressure.

2.3. *Characterization of nanofiber paper-like sheets*

Paper-like sheets were obtained by filtration of fibrillated nanofiber suspensions and subsequent drying at 110°C and slight pressure in a hot-press. The commercial cellulose nanofiber used as control was Celish KY-100G (Daicel Corporation, Japan), produced by a high-pressure homogenizer, and consisting of a slurry with 10 wt% nanofiber content. Ribbon-shaped test pieces 70 mm x 6 mm were cut from the nanofiber sheets and subjected to tensile test with an Instron 5567 universal materials testing machine at a

strain rate of 1.0 mm/min and a gage length of 50 mm. The tensile properties are the average of 10 replicates.

The surfaces of nanofiber sheets were observed using a field emission scanning microscope, model S-4700 (Hitachi High-Technologies Corporation, Japan). The accelerating voltage was set to 1.5 kV, and the samples were coated with platinum to avoid specimen charging.

3. Results and Discussion

The grass-derived pulp fibers had lignin and hemicelluloses extracted by a chemical pre-treatment and blended for 10 min. under reduced pressure. The pulp fibers were kept wet until fibrillation as drying would cause the formation of irreversible hydrogen bonds between the nanofibers that eventually would prevent their proper individualization [6]. We have assessed possible approaches to enhance fibrillation efficiency, shortening treatment times, and reducing energy consumption by designing a new bottle with features suited for fibrillation. The redesigned bottle has the following features:

1. Downsized bottle to half capacity from 2 L to about 1L;
2. Square cross section to achieve turbulent flow during blending;
3. Heat dissipation by a double-walled aluminum bottle with water circulation for long time continuous blending;
4. Possibility of evacuating air from the bottle for blending at reduced pressure.

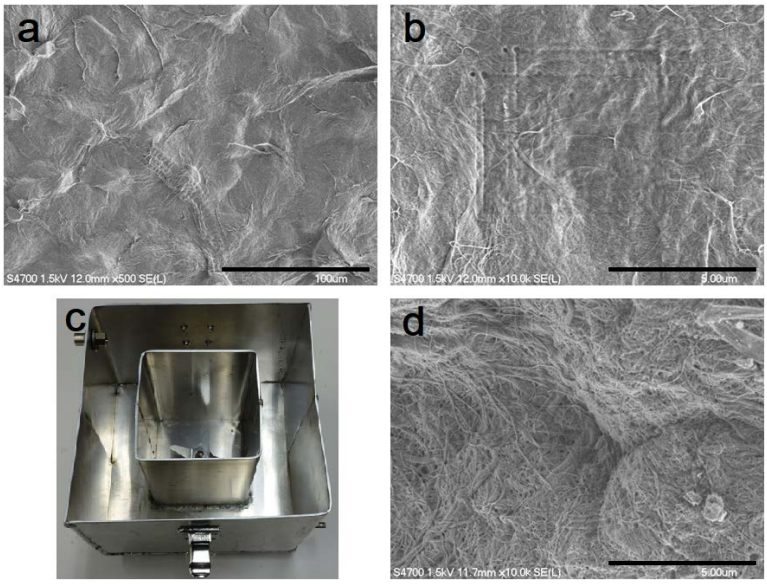

Fig. 1. Scanning electron micrographs of: (a) sudachi nanofiber, scale bar 100 μm; (b) sudachi nanofiber, scale bar 5 μm; (c) modified blender bottle; (d) commercial nanofiber Celish, scale bar 5 μm.

The volume reduction and turbulent flow blending were intended to increase the probability of fiber collision with the rotating blades. Cooling of the bottle is indispensable as continuous blending over just 5 minutes increases the temperature of the

blending medium up to the boiling point of water. Air evacuation is still under consideration but it seems to work in the case of fibrillation of sudachi residue pulp. As it consists basically of parenchyma cells that are easier to fibrillate, the aqueous suspension turns highly viscous after short blending time. Reduced pressure apparently prevents air pockets and promptly collapses them if formed, increasing the collision rate of parenchyma cells against the blades.

Paper-like sheets of obtained nanofibers were subjected to tensile test. The larger exposed surface area of nanofibers produces higher sheet strength, whereas not completely nanofibrillated nanofiber bundles act as defects, reducing the sheet strength. These balancing effects make the tensile strength of the sheets an indirect evidence of the overall quality of the produced nanofibers.

Table 1. Tensile properties of cellulose nanofibers obtained by blending at reduced pressure.

Raw material	Tensile strength (MPa)	Strain at fracture (%)	Tensile modulus (GPa)
Grass	60 ± 5	3.5 ± 0.4	5.7 ± 0.7
Sweet potato vine	88 ± 6	3.8 ± 0.6	6.7 ± 0.3
Sudachi residue	135 ± 8	9.5 ± 0.6	6.5 ± 0.2
Sudachi residue (1 atm)[a]	125 ± 6	4.7 ± 1.2	8.8 ± 0.6
Celish (commercial CNF)	63 ± 3	4 ± 1	7.1 ± 0.5

[a]Blended under atmospheric pressure.

Figure 1a shows the sudachi nanofiber paper at low magnification with no visible remaining thick fibril bundles. Figure 1b at higher magnification shows the tiny nanofibers that are comparable in size to the commercial nanofibers shown in Fig. 1d.

4. Conclusion

The proposed fibrillation by blender produced nanofiber paper that compares favorably in strength to the commercial nanofiber paper. In particular sudachi residue produced significantly stronger and tougher paper when fibrillated by blending at reduced pressure.

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