Obtaining Cellulose Nanofibers with a Uniform Width of 15 nm from Wood

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Introduction

As described in some comprehensive reviews, the fabrication of nanofibers, generally defined as fibers with a diameter below 100 nm,[1,2] is presently the subject of much attention because of their unique characteristics such as a very large surface-to-volume ratio[3] and the formation of a highly porous mesh[4] as compared with other commercial fibers. Therefore, these nanofibrous materials are prime candidates for many momentous applications such as reinforcement in nanocomposites, tissue engineering scaffolds, and filtration media.[5] A large number of synthesis and fabrication methods for producing these nanofibers have already been reported. In particular, electrospinning has been the subject of much attention over the past decade.

It is well-known that nanofibers are produced in nature, for example, collagen fibrils in tendons and ligaments and silk fibroin. Among the variety of natural nanofibers, cellulose microfibrils, which are the major constituent of plant cell walls and are also produced by some bacteria, are the most abundant natural nanofiber on earth. The microfibrils, having a width ranging from 5 to 30 nm,[6] are highly crystalline materials formed by laterally packing long cellulose molecules with hydrogen bonding. The resultant stable structure has outstanding mechanical properties, including a high Young's modulus (138 GPa in the crystal region along the longitudinal direction)[7] and a very low coefficient of thermal expansion (10^{-7} K^{-1} along the longitudinal direction).[8] Therefore, cellulose whiskers and fibrils have great potential for use as reinforcement in nanocomposites and have attracted a great deal of interest recently.[9−13]

In addition to their exceptional mechanical properties, cellulose nanofibers have been shown to be an ideal reinforcement of transparent resins since they are free from light scattering due to their diameters being less than one-tenth of the visible light wavelength.[14] Recently, Yano et al. developed transparent and flexible nanocomposites using bacterial cellulose (hereafter referred to as BC) nanofibers 50 nm in width.[15] The composites are optically transparent at fiber contents as high as 70% in conjunction with a very low coefficient of thermal expansion and high strength. Furthermore, because of the size effect of the reinforcement, high transparency is obtained against wider distributions of ambient temperatures or refractive indices from various matrix resins,[16] expanding the potential applications in optoelectronic devices.

Since plant-based cellulose nanofibers have the potential to be extracted into fibers thinner than BC, many researchers have been extensively studying the extraction of nanofibers from wood and other plant fibers. In cell walls, cellulose nanofibers are embedded in matrix substances such as hemicellulose and lignin, and, up unto this time, the removal of the matrix substances has been performed before the fibrillation process. Bleached pulps are often used in order to skip the matrix removal process.[17,18] The fibrillation of plant fibers has mainly employed mechanical treatments using a high-pressure homogenizer,[17] a grinder,[19,20] cryocrushing,[18,21] or, recently, ultrasonic[22] and enzymatic methods.[23] However, because of the complicated multilayered structure of plant fibers and the interfibrillar hydrogen bonds, the fibrils obtained by these methods are aggregated nanofibers with a wide distribution in width. Saito et al. reported that TEMPO-mediated oxidation on the surface of the microfibrils assisted the homogenizing mechanical treatment and enabled them to obtain nanofibers with a uniform width of 3−5 nm, although the nanofibers are actually cellulose derivatives.[24] Here we report on an efficient extraction of wood cellulose nanofibers as they exist in the cell wall, with a uniform width of 15 nm, by a very simple mechanical treatment.

Experimental Section

In cell walls, cellulose microfibril bundles 12−16 nm in width exist encased by the embedding matrix.[25,26] However, the drying process in typical pulp production generates strong hydrogen bonding between the bundles after the removal of the matrix, which seems to make it difficult to obtain thin and uniform cellulose nanofibers. Hence we kept the material in the water-swollen state after the removal of the matrix.

Wood powder from Radiata pine (*Pinus radiata* D. Don) sieved under 60 mesh was used for this study. First, solvent extraction was performed in a Soxhlet apparatus with a 2:1 mixture of toluene/ethanol for 6 h. Second, lignin in the sample was removed using an acidified sodium chlorite solution at 70 °C for an hour, and the process was repeated until the product became white.[27] Third, the sample was treated in 6 wt % potassium hydroxide over night at room temperature and then at the same concentration at 80 °C for 2 h in order to leach hemicelluloses. This resulted in whole cellulose being practically obtained, and the α-cellulose content, which was measured following the method of Loader et al.,[28] was more than 85%. In Figure 1b, individualized microfibril bundles approximately 15 nm wide could be seen. However, as the sample still maintained the initial cell shape shown in Figure 1a, we finally passed the slurry of 1 wt % purified cellulose through a grinder (Masuko Corp.) at 1500 rpm.[19,20]

The fibrils obtained were subjected to freeze-drying or oven-drying at 105 °C. These specimens were platinum coated in an ion sputter coater and observed on a JEOL JSM-6700F field emission scanning electron microscope (FE-SEM). Although the coating thickness was approximately 2 nm in this condition, we confirmed that the coating did not change the lateral dimension of the fibrils significantly because the ions are sputtered from the top.

Results and Discussion

Interestingly, the slurry after one pass through the grinder exhibited a remarkably high viscosity, suggesting that the homogeneous dispersion of hydrophilic cellulose nanofibers with a high surface-to-volume ratio in water was accomplished. Figure 2 shows SEM images of (a) the freeze-dried and (b,c) oven-dried 0.2 wt % slurry. All images show continuous nanofibers with a uniform diameter of approximately 15 nm, forming a very fine network. A remarkable outcome of this new nanofiber extraction method can be seen in Figure 2c. Thicker fibrils were not observed anywhere within the extensive area of 2 μm × 2.5 μm. It should be emphasized that the width of nanofiber extracted in this study corresponds to that of the microfibril bundles in Figure 1b, indicating that the never-dried

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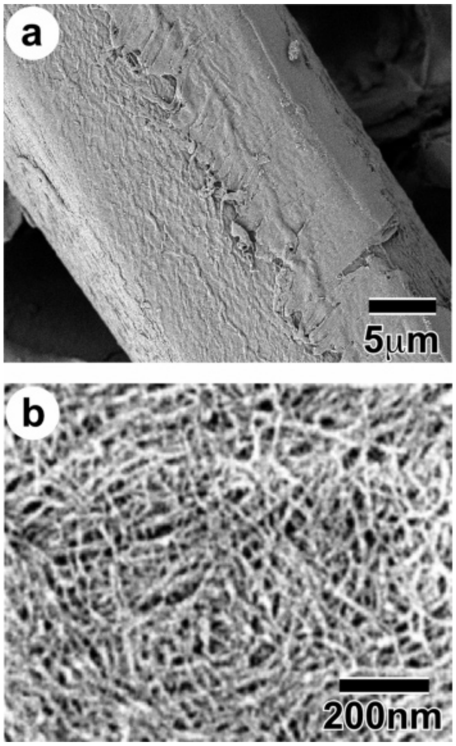

Figure 1. FE-SEM micrographs of (a) a wood fiber (× 3000) and (b) the surface of the wood fiber (× 30 000) after removing lignin and hemicellulose.

process enables the extraction of the natural nanofibers as they exist in wood cell walls by a simple mechanical treatment.

To substantiate the uniformity and fineness of the nanofibers, we produced nanocomposites with acrylic resin using the nanofiber as a filler, according to the method by Iwamoto et al.[20] The thickness and the fiber content of the obtained nanocomposite were 50 μm and 60 wt %, respectively. Figure 3a demonstrates the regular light transmittance spectra of the nanocomposite, compared with that of the nanocomposite made with BC, which was produced by impregnating the same acrylic resin in a hot-pressed BC sheet.[15,16] Also of note, the regular transmittance of this nanocomposite is higher than that of the BC nanocomposite in the visible wavelength range and at the same thickness and filler content. This confirms that the nanofibers obtained from wood in this study are more uniform and far thinner than BC, as shown in Figure 3b,c. The coefficient of thermal expansion from 20 to 150 °C was as low as 13 ppm/K, which is one-seventh of that of the neat acrylic resin, thus suggesting that the fine network of the nanofibers with a high aspect ratio contributes to its high reinforcing efficiency.

Furthermore, the nonwoven nanostructures shown in Figure 2 associated with interconnected pores and a very large surface-to-volume ratio imply the potential utilization of the nanofiber sheets for membranes, tissue scaffolds, filters, and so on. Ma et al. reported on the feasibility of applying regenerated cellulose nanofiber membranes prepared by electrospinning as affinity membranes.[29] Given the bonus of high flexibility in surface functionalities inherent to cellulose, such attributes would open further potential applications.

Conclusion

The grinding treatment in an undried state after the removal of the matrix substance has shown to be effective to obtain cellulose nanofibers with a uniform width of approximately 15 nm. This study demonstrates a powerful yet quite simple method for the production of the nanofibers from plant fibers. More stable mass production of the nanofibers can be realized because this method is applicable to any natural fiber resource containing lignin such as flax, sugarcane bagasse, and wheat straw. We

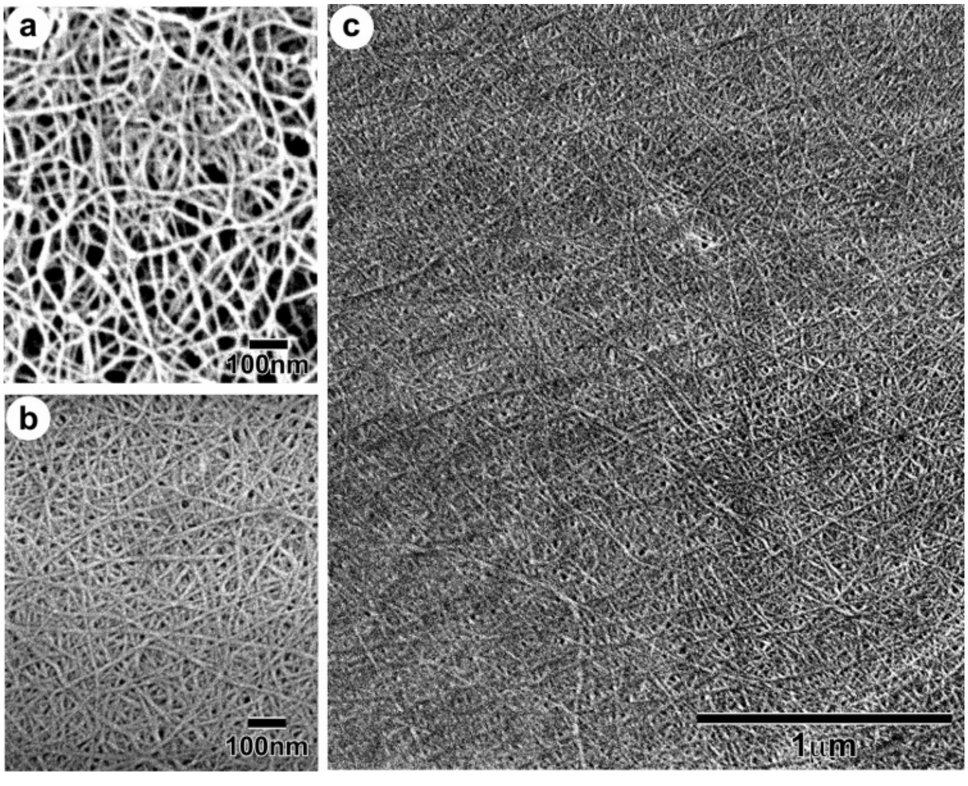

Figure 2. FE-SEM micrographs of (a) freeze-dried nanofibers (× 60 000), (b) oven-dried nanofibers (× 60 000), and (c) oven-dried nanofibers (× 20 000) after one pass through the grinder.

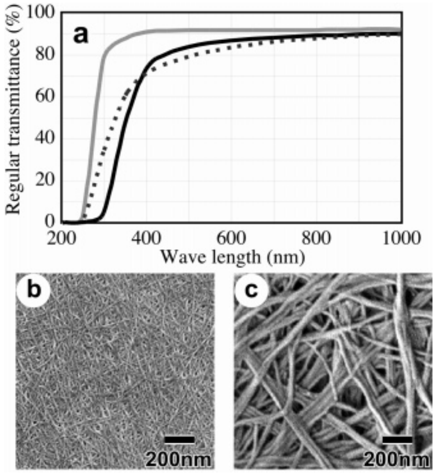

Figure 3. (a) Regular light transmittance of the nanocomposite made from wood (black line), the nanocomposite made from BC (dashed line) and a neat acrylic resin sheet (gray line). All samples were 50 μm in thickness. Also shown are FE-SEM micrographs (× 30 000) of (b) the wood nanofiber sheet and (c) the BC nanofiber sheet, both before impregnating the acrylic resin.

hoped that the results in this study will further stimulate interest in environmentally friendly natural nanomaterials.

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