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Morphology of Nanocelluloses and Micro-sized Cellulose Fibers Isolated by Acid Hydrolysis Method

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ABSTRACT

As a part of utilizing the nanocellulose (NC) from lignocellulosic components of wood biomass, this paper reports preliminary results on the products of sulfuric acid hydrolysis. The purpose of this study was to investigate the morphology of both NC and micro-sized cellulose fiber (MCF) isolated by acid hydrolysis from commercial microcrystalline cellulose (MCC). Field emission - scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM) were employed to observe the acid hydrolysis suspension, NC, and MCF. The electron microscopy observations showed that the acid hydrolysis suspension, before separation into NC and MCF by centrifugation, was composed of nano-sized NCs and micro-sized MCFs. The morphology of isolated NCs was a whisker form of rod-like NCs. Measurements of individual NCs using TEM indicated dimensions of 6.96 ± 0.87 nm wide by 178 ± 55 nm long. Observations of the MCFs showed that most of the MCC particles had de-fibered into relatively long fibers with a diameter of 3 - 9 μm, depending on the degree of acid hydrolysis. These results suggest that proper technologies are required to effectively realize the potentials of both NCs and MCFs.

Keywords: Morphology, Nanocellulose, Micro-sized cellulose fiber, Acid hydrolysis, FE-SEM, TEM

1. Introduction

In recent years, the use of natural fibers for reinforcement of polymers and composites has attracted much attention due to environmental concerns. Among the natural fibers, cellulose is the most abundant, renewable, and biodegradable natural polymer. Cellulose fibers are present in the cell walls of plants in combination with hemicelluloses, lignin, waxes, etc., commonly known as nano-sized microfibrils. These nano-sized fibrils are further composed of crystalline and amorphous regions. The crystalline region consists of bundles of microfibrils in which the cellulose chains are stabilized laterally by hydrogen bonds between hydroxyl groups. Thus, they have high structural strength and stiffness. It has been reported that the elastic modulus of e-glass fiber is 73 GPa (1); in contrast, the elastic modulus of native cellulose Ⅰ crystal regions is 167.5 GPa (2) and that of tunicin whiskers is 143 GPa (3). Due to these strong

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mechanical properties, nano-cellulose has generated a great deal of interest as a source of nano-sized reinforcement.

Various methods, including chemical and mechanical treatments, have been used to isolate cellulose microfibrils from a variety of sources. Chemical methods such as acid hydrolysis remove the amorphous regions of cellulose fibers and produce nano-sized fibrils. Wood pulp (4), marine animals (5), sisal (6), sugar beet pulp (7), and microcrystalline cellulose (MCC) (8) have been used as raw materials for isolating nanocellulose (NC) through acid hydrolysis. Mechanical methods include high-pressure homogenization (9), freeze-drying and cryocrushing (10), and high-intensity ultrasonication (11).

Fibrils produced by these mechanical methods may be bundles of microfibrils or cellulose nanofibers. The published literature indicates that NCs have a wide range of sizes, depending on the preparation method and source of raw materials (12−16).

Although many studies have been done on NCs, there have been few studies of the morphology of NCs, in particular, morphological comparisons of the NCs and the micro-sized cellulose fibers (MCF) that are found in the sediment of acid hydrolysis. Thus, this study investigated the morphology of the NCs and MCFs using both field emission−scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM).

2. Materials and methods

2. 1. Materials

Commercially available MCC (Avicel® PH-101; Fluka Chemical Corp., Milwaukee, WI, USA) was used as the raw material for isolation of the NCs. Sulfuric acid (95%; DC Chemical Co. Ltd., Seoul, Korea) was used for acid hydrolysis of the MCC.

2.2. Preparation of the NC and MCF

About 10 g MCC was mixed with 100 mL deionized water. The water/MCC suspension was then placed in an ice bath under continuous mechanical stirring, and 100 mL sulfuric acid was added by drops. The suspension was then hydrolyzed at 44 ºC for 130 min. The suspension was then washed with deionized water for 20 min at 5000 rpm with repeated centrifugation (Hanil Centrifuge Co., Ltd, Incheon, Korea). The supernatant was removed from the sediment, replaced with fresh deionized water, and mixed. The centrifugation step was continued until the pH of the surfactant was 1. The final wash was conducted using dialysis with deionized water to remove the last residues of sulfuric acid until the wash water was maintained at a constant pH of 4. Before observation with the microscope, the supernatant (the NC solution) and the sediment (containing the MCFs) were freeze-dried at -50 °C and 5 mTorr.

2. 3. Microscopic observation

An FE-SEM (S-4300 and EDX-350; Hitachi, Tokyo, Japan) was used to observe the three-dimensional morphology of the MCC particles, acid hydrolysis suspension, NCs, and MCFs. The MCC powder was attached to carbon tape and observed at an accelerating voltage of 15 kV after gold coating. Both the freeze-dried NCs and MCFs were diluted in distilled water to a concentration of 1 wt%. Three drops of the diluted solution were placed on the center of a cover glass. The samples were then dried in a vacuum oven (281A; Fisher Scientific, Suwanee, GA, USA) at 50 ºC overnight. After gold coating, the images of the NCs and MCF samples were taken at an accelerating voltage of 10kV and 5kV respectively.

TEM (H-7600; Hitachi) observations were performed at an accelerating voltage of 100 kV for the acid suspension and NC samples. TEM observation was not conducted for the MCF samples. The samples were diluted in distilled water to a concentration of 0.5 wt%. To examine the morphology of the NCs ,3 droplets of

the suspension were placed on a copper grid coated with a thin carbon film and were allowed to dry at 70 ºC for 10 min. To enhance the contrast in the TEM, the NCs were stained by allowing the grids to float in a 3 wt% solution of uranyl acetate for 3 min and then drying at 70 ºC for 10 min. The width and length of the NCs were measured for at least 10 individual NCs from the TEM micrographs.

3. Results and discussion

3. 1. Morphology of the MCC

As noted above, commercial MCC was used as the raw material for acid hydrolysis in this study. To evaluate the state of the raw material, the morphology of the MCC powder prior to acid hydrolysis was observed using FE-SEM. Fig. 1 shows that the MCCs were mixtures of both aggregated and roughly spherical particles (white arrow) and fiber bundles of wood cell elements (black arrow) of different sizes. These findings are similar to previous results (17). The particle size of the MCC was 14−35 μm (based on the manufacturer's data). The morphology of the MCC particles required breakage of the aggregated spherical particles and fiber bundles during acid hydrolysis.

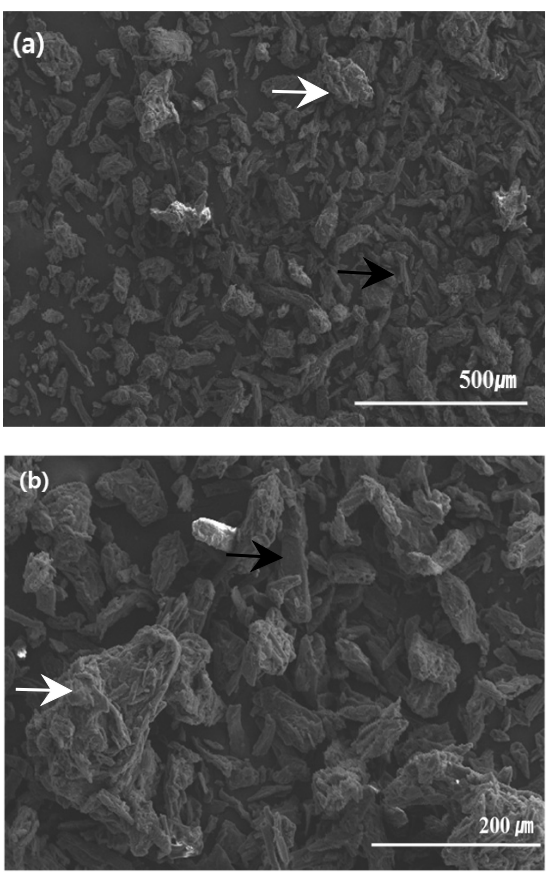

Fig. 1. FE-SEM images of the MCC.
(a) x80, (b) x200.

3. 2. Morphology of the NCs and MCFs in the suspension

The MCC powder was hydrolyzed using sulfuric acid to obtain the NCs and MCFs. To evaluate the morphology of the NCs and MCFs in the suspension after acid hydrolysis, both FE-SEM and TEM were used to observe the suspension prior to separation of the NCs and MCFs by centrifugation. Fig. 2 shows FE-SEM images of the suspension at various magnification levels. As shown in Fig. 2, both NCs (white arrows) and MCFs (black arrows) were observed. However, it was difficult to clearly observe the NCs and MCFs using the FE-SEM. Thus, TEM was also used to observe the suspension.

Fig. 3 shows TEM images of the suspension at various magnification levels. As expected based on the FE-SEM results, under TEM observation, the images of the suspension clearly show both NCs (white arrows) and MCFs (black arrows). Although the MCC particles were acid-hydrolyzed, the suspension still contained many large-diameter, long fibers (black arrows in Fig. 2). The average width of these fibers was 88.4 ± 29 nm (n=10). Apparently, these fibers are aggregates of microfibril-sized structures. For example, the average cross-sectional diameter of microfibrils has been reported as 10−12nm (18); Donaldson(2007) also reported that the fibrillar structure of the secondary wall varied from microfibril-sized structures of 3−4nm up to large aggregates 60nm

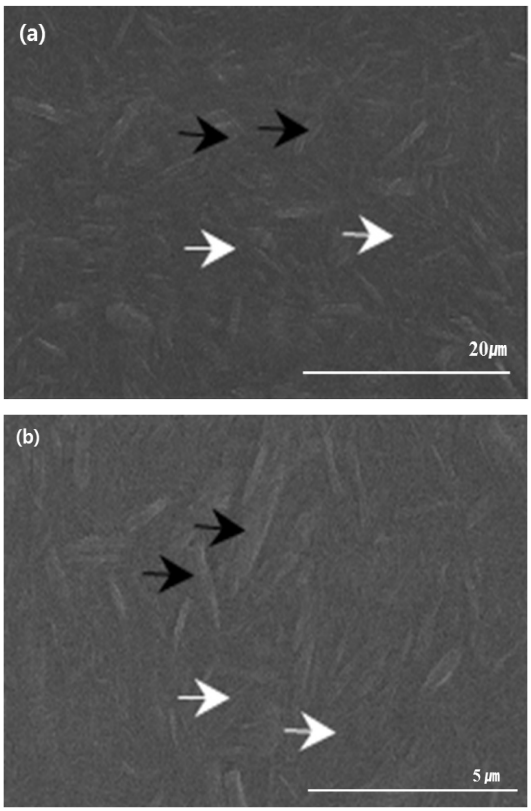

Fig. 2. FE-SEM images of the suspension. (a)×5000, (b)×10000.

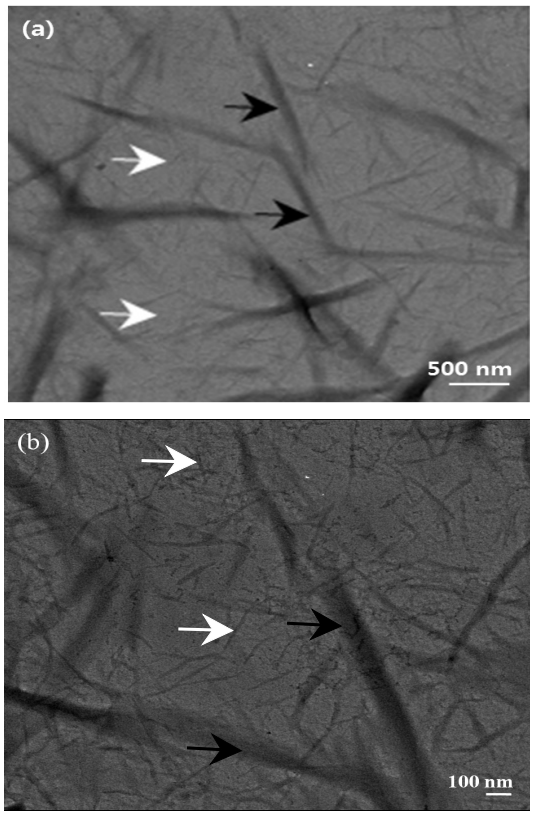

Fig. 3. TEM images of the suspension. (a)×5000 and (b)×10000

in diameter (19).

3. 3. Morphology of the isolated NCs

Fig. 4 shows FE-SEM images of the NCs (white arrows) isolated by centrifugation of the acid hydrolysis suspension at various magnification levels. Because the NCs were prepared by drying a dilute solution of the NCs in distilled water, the observed N Cs were covered with a water layer (Fig. 4b). FE-SEM observation was not sufficient to definitively identify the NCs.

However, a particular type of NC was observed by FE-SEM among the isolated NC samples at various magnification levels (Fig. 5). Fig. 5 shows many closely packed micro-fibrillated cellulose bundles. Measurement of these microfibrils indicated an average width of 83 ± 19 nm, within the range of large aggregates of cellulose crystalites (19). This morphology type for cellulose fibers has previously been reported for NCs from grass (20).

The authors explained that the close packing of the microfibrils had occurred through two different means, the presence of residual cementing materials and electrostatic attraction (20).

TEM images of the NCs separated by centrifugation of the acid hydrolysis suspension are shown in Fig. 6 at various magnification levels. The NCs (white arrows) were clearly identified in these images, with a rod-like whisker form

composed of an aggregate of a few NCs. This agglomeration could be due to the water used for sample preparation (8). Analysis of the TEM images

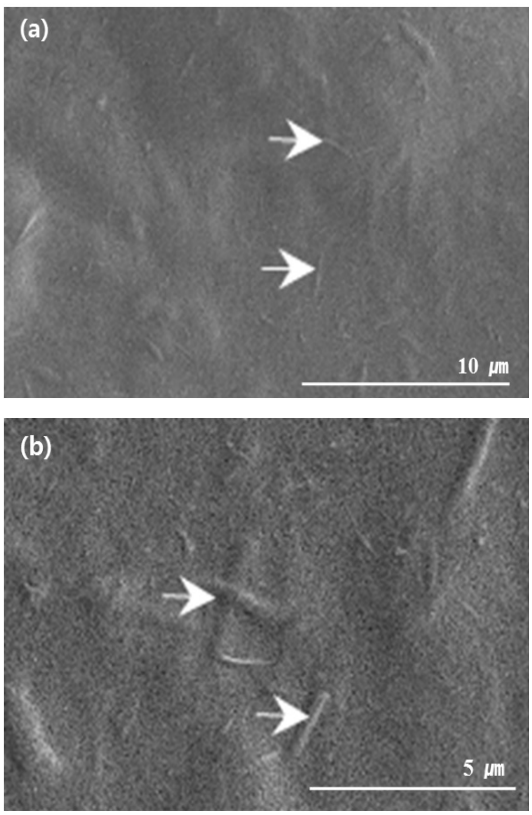

Fig. 4 FE-SEM images of the NCs at various

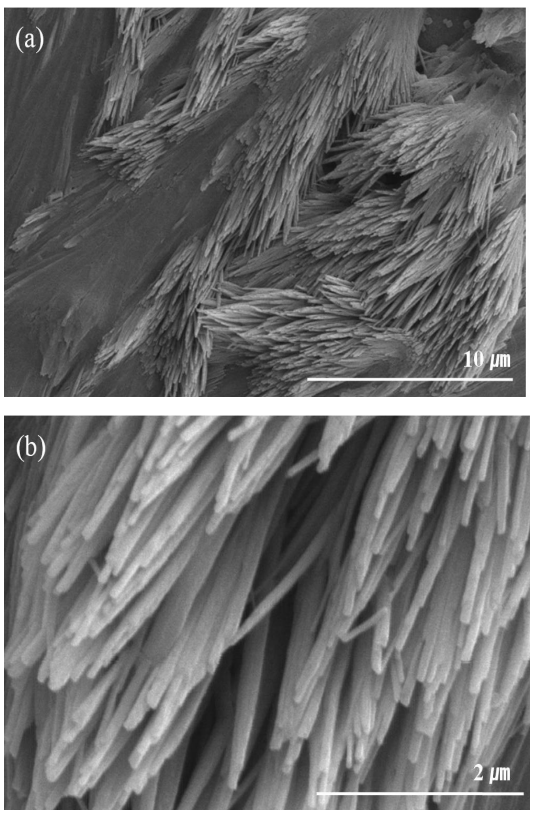

Fig. 5. FE-SEM images of the NCs at various magnification levels.
(a)×5000 and (b)×25000.

determined that the isolated NCs had a width (d) of 6.96 ± 0.87 nm and a length (L) of 178 ± 55 nm, giving an aspect ratio (L/d) of ~25. These results are in close agreement with previous published results (8, 21). For example, Dong et al.(1996) reported that the isolated NCs in their study were 70−170 nm long and 7nm wide(21).

3. 4. Morphology of the isolated MCFs

Isolation of the NCs after acid hydrolysis left a cellulosic fiber residue (or sediment). Despite the excellent reinforcement qualities of the NCs, utilization of the sediment remaining after acid hydrolysis is equally important in terms of raw materials. Therefore, we observed the morphology of the sediment or residues.

Fig. 7 shows FE-SEM images of the freeze-dried MCFs. Compared to the MCC, the MCFs were much smaller in size. The smaller size of the MCFs was clearly due to acid hydrolysis, which had removed the lignin between the microfibrils as well as the cell walls. However, FE-SEM observation also indicated the presence of large-diameter fibers (black arrows) as well as micro-sized fibrillar structures (white arrows) (Fig. 6). These images also showed that the large-diameter fibers had a much smoother surface than those of the MCC particles as a result of the acid hydrolysis.

Measurement of these fibers determined a diameter of 3−9 μm, in the micro-sized range. These results indicate that the morphology and dimensions of the

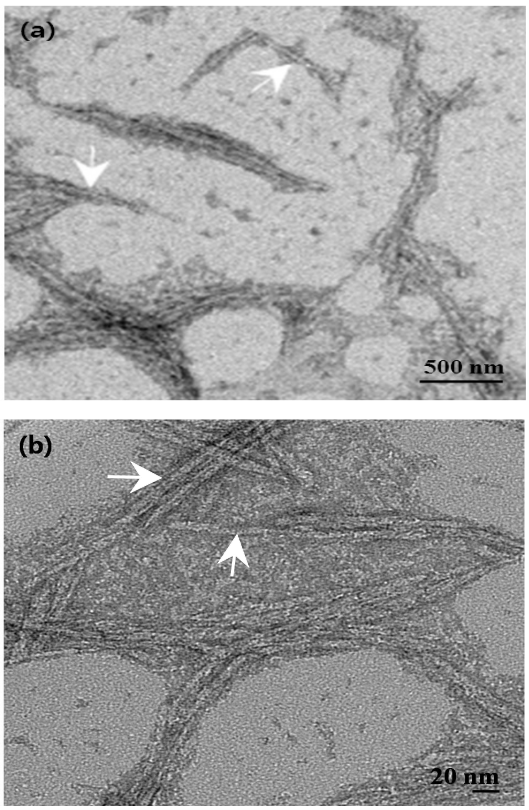

Fig. 6. TEM images of the NCs at various magnification levels. (a)×30000 and (b)×50000.

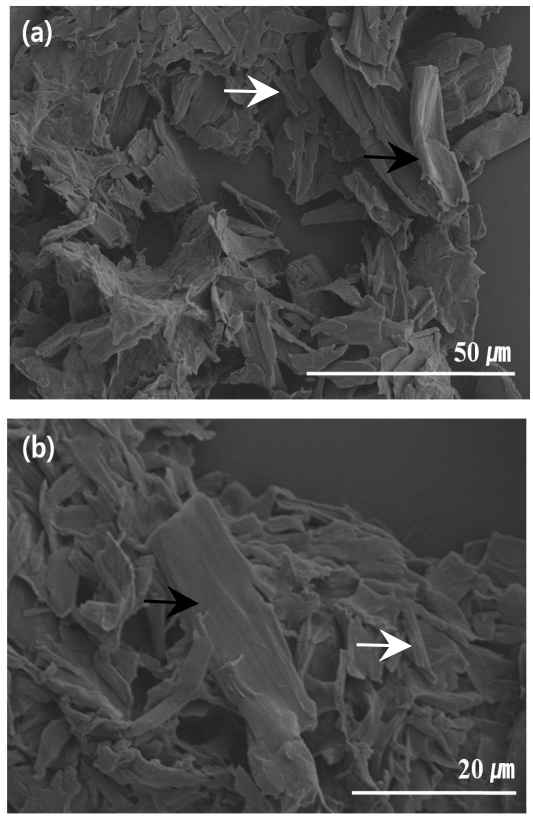

Fig. 7. FE-SEM images of MCF at various magnification levels. (a)×1000 and (b)×2000.

MCFs can be used as an indicator of the degree of acid hydrolysis. The yield of NCs in this study was 9.7%, lower than in a previous study (8).

4. Conclusions

In this study, both NCs and MCFs were isolated by sulfuric acid

hydrolysis from MCC. The morphologies of the acid hydrolysis suspension, NCs, and MCFs were investigated using FE-SEM and/or TEM. Both the FE-SEM and TEM results showed that the acid hydrolysis suspension was composed of NCs and MCFs. The TEM results

showed that the NCs had a rod-like whisker form with a width of 6.96 ± 0.87 nm and a length of 178 ± 55 nm. The FE-SEM results also identified a particular type of NC, closely packed together with a width of 83 ± 19 nm. The FE-SEM observation results for the MCFs showed that they had micro-sized diameters of 3–9 μm. These results indicate that different technologies and approaches are required to efficiently maximize the potential of both NCs and MCFs for future applications.

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