A Study on Fabrication of Cellulose Nanofibers in Water using a Microfluidizer

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ABSTRACT

Cellulose nanofibers (CNFs) were successfully fabricated by fibrillation of wood pulp cellulose into submicron and/or nanoscale nanofibers with a microfluidizer in water. CNFs have the great potential as reinforcing materials for polymeric composite materials due to their excellent mechanical and functional properties. The microfluidizer generated high shear fluid in fiber slurries to give rise to the disintegration of cellulose into the formation of CNFs through shear, impact and cavitation in an interaction chamber. This study investigated the effects of processing conditions of the microfluidizer (nozzle diameter, flow pressure, path number and nozzle setup configuration) on the morphology and properties of the resultant CNFs and nanopapers. The microscopic study showed that the increase in the operating pressure and pass number manifestly reduced the CNF diameter. Most CNFs, experiencing the complete fibrillation process (10 pass at 10000psi, 10 pass at 30000 psi, and 10 pass at 45000 psi), were found less than 50 nm in fiber diameter. In addition, the fibrillation led to the removal of amorphous region such as lignin and amorphous cellulose, which can account for the increase in the crystallinity index. The immense surface area and the nanoscale dimensions of nanopaper can lead to the emerging materials for reinforcements in polymer composites, differentiating from classic microcomposites and providing the opportunity for nanoengineered materials that could have not been achieved from conventional materials.

Keywords: cellulose, nanofiber, nanocomposite, nanopaper, nano/micro fibrilliation,

1 INTRODUTION

Over decades, intensive research of nanotechnology has been conducted to characterize the physical and mechanical properties, improve functions of nanocomposite systems, and develop processing technologies for nanomaterials. It would open up new era of revolutionary materials. The promise of nanotechnology lies in multi-functionality that could have not been achieved from conventional materials. For example, the addition of rigid inorganic micro-sized fillers in polymer matrices increases stiffness and strength. However, it would offset ductility and toughness of polymers due to fillers that cause stress concentration. Well-dispersed nanofillers, on the other hand, improve modulus and strength of polymer matrices while maintaining or even increasing ductility and toughness by breaking up the strength-toughness relationship of the current engineering materials. It is because nano-sized fillers may not be subjected to stress concentration. Accordingly, nanocomposites become of great importance in the academic and commercial research fields [1].

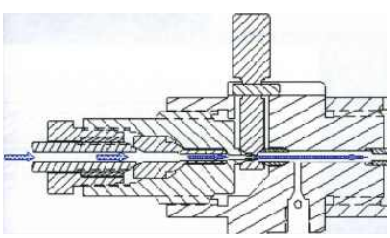
Cellulose is the most abundant biopolymer on earth, and the main reinforcing constituent in plant cell walls. It is aligned poly-β(1,4)-D-glucan molecules in extended chain conformation assembled into microfibrils or nanofibrils of high modulus and strength [2]. The nanofibril cellulose (NFC) or cellulose nanofibers (CNFs) have a dimension of typically 5-10 nm in diameter and several micrometers in length. They are not only strong and stiff but also can offer the opportunity for eco-friendly and sustainable bio-materials from renewable resources. Their modulus and strength are 134 GPa and 4 GPa, respectively, which are superior to glass fibers and compared with aramid fibers. The high aspect ratio and excellent properties have led to the emerging materials for reinforcements in polymer composites.

Cellulose nanofibers were successfully prepared by high pressure homogenization with a microfluidizer in the previous studies [2, 3]. After enzymatic and mechanical beating pretreatment of cellulose pulps, the mechanical homogenization can fibrillize the cellulose into nanofibrils by subjecting micro-sized cellulose fibers into high shear forces. However, to the authors' knowledge, the effects of the processing conditions of the microfluidizer (nozzle diameter, flow pressure, pass number, and nozzle setup configuration) have not been fully understood. In the present study, the effects of the processing conditions of the microfluidizer were systematically investigated on the morphology and properties of the resultant CNFs and nanopapers by wet-laid paper-making method in order to fully realizes the potential of CNFs and identify opportunities regarding the future directions of CNFs and their nanocomposites.

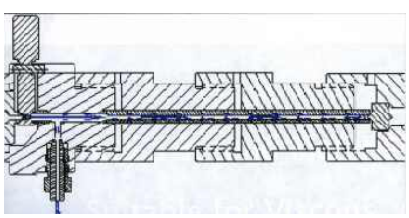
2 EXPERIMENTAL

2.1 Preparation of cellulose nanofibers

Cellulose pulps (Whatman International, Ltd., England) were used to prepare the fiber slurry by dispersing the pulp in distilled water at a solid weight content of 0.5% using an overhead mixer for 30 minutes. The resulting slurry was subject to high pressure homogenization to fibrillize the cellulose fibers. The homogenization of the slurry was performed by a microfluidizer (MinideBee, Bee International, USA) with parallel flow and reverse flow nozzle setup configurations, as shown in Figure 1. In each nozzle setup, the slurry was totally passed 30 times through the microfluidizer with various nozzles sizes and at various operating pressures. The first ten passes were carried out a operation pressure of 10,000 psi with a nozzle of 10/1000'' diameter, and then the second ten passes at a operation pressure of 30,000 psi with a nozzle of 8/1000'' diameter and the last ten passes at a operation pressure of 45,000 psi with a nozzle of 5/1000'' diameter. Samples were collected every 10 passes for the characterization of CNFs, and the samples were designated as the following example. The sample, experiencing the complete fibrillation process at the parallel flow nozzle configuration, was designated as the sample code of W-5-45000-10, where nozzle setup configuration (W: parallel, A: reverse)-nozzle diameter-operating pressure-pass number are placed in order.



(a)



(b)

Figure 1: The nozzle setup configuration: (a) parallel flow and (b) reverse flow [4].

2.2 Preparation of cellulose nanopapers

After homogenization process, cellulose nanopaper was prepared by vacuum filtration wet-laid process of the CNF slurries using a 100 mm-diameter glass funnel fitted with 1000 grade stainless steel mesh. The stacked nanopaper and steel mesh was dried at 80°C for 24 hours in a convection oven at ambient pressure. After drying, the nanopaper thickness is approximately around 0.01mm.

2.3 Characterization

The particle size in fiber slurries was measured by a laser particle size analyzer (Mastersizer Micro, Malvern, UK). The lateral dimension of CNFs and the morphology of nanopapers were analyzed by field emission-scanning electron microscope (FE-SEM, Quanta 200, FEG, Netherland). Wide-angle X-ray diffraction (WAXRD) analyses were performed with a Rigaku MiniFlex™ II diffractometer at 30kV and 15mA. The diffraction patterns were taken by the radiation of Cu Kα perpendicular to the nanopaper surface. The crystallinity index (CI) was calculated by the following equation [5]:

$$CI = \frac{(I_{(002)} - I_{(am)})}{I_{(002)}} \quad (1)$$

where $I_{(002)}$ is the counter reading at peak intensity at a 2θ close to 26° representing the crystalline materials and $I_{(am)}$ is the counter reading at peak intensity at a 2θ close to 18° representing the amorphous materials. Tensile tests for the nanopapers were performed at a crosshead speed of 10 mm/min on a universal testing machine (Tinius Olsen, England) with specimens of 63 mm length and 10 mm width, and a gauge length of 40 mm.

The specific surface area of the fibril nanopapers was determined using Congo red dye absorption method [6]. A 5 mg nanopaper sample in a phosphate solution (pH 6) was dyed with various concentration of Congo red ranging from 0.01mg/ml to 0.16mg/ml at 30°C for 90 minutes by a shaker. The suspension was filtered and the final dye solution was used to determine the dye concentration by its UV-VIS absorbance at 500nm with a spectrophotometer (Cary 500, Varian, Australia). The absorbed amount of Congo red on the nanopaper surface was calculated by the Langmuir equation (Eq. 2) and a plot of *1/A* versus *1/C* [6]:

$$\frac{1}{A} = \left(\frac{1}{K_{ads}[A]_{\max}}\right)\left(\frac{1}{C}\right) + \left(\frac{1}{[A]_{\max}}\right) \quad (2)$$

where A is the amount of dye absorbed by substrate [mg dye/mg substrate], C is the amount of dye not absorbed [mg/mL], $[A]_{max}$ is the maximum amount of dye absorbed by substrate [mg/g], and K_{ads} is the equilibrium constant. The specific surface area (SSA) of the cellulose sample was determined by the following equation [6]:

$$SSA_{substrate} = [A]_{\max} \times N_A \times SA_{CR} / CR \quad (3)$$

where N_A is the Avogadro constant (6.022×10^{23} mol^{-1}), SA_{CR} is the surface area of a molecule of Congo red (1.73 nm^2), and CR is the molecular weight (696.7 g/mol) of Congo red.

3 RESULTS AND DISCUSSION

The particle size of the cellulose materials was summarized in Table 1. It is clearly seen that the particle size decreases with decreasing the nozzle size, and increasing the operation pressure and the pass number. The high pressure homogenization process was originally developed by Herrick et al. [7] and Turbak et al. [8] to produce microfibril/nanofibril cellulose. The mechanical process by a microfluidizer generates high shear force on fiber slurries to give rise to the fibrillation of cellulose in an interaction chamber through shear, impact and cavitation, leading to the formation of CNFs. As shown in Table 1, the reverse flow nozzle setup is more effective to facilitate the reduction of the cellulose size than the parallel flow due to the more possibility of impact in an interaction chamber.

Sample code	Size [μm] (v=0.5)*	Size [μm] (v=0.9)*
Virgin	208.8	307.48
W-10-10000-10	172.48	241.17
W-8-30000-10	126.74	233.05
W-5-45000-10	41.08	97.57
A-10-10000-10	67.66	305.7
A-8-30000-10	48.95	139.58
A-5-45000-10	36.31	88.18

*v: particle volume fraction

Table 1: Particle size (mean diameter) of cellulose slurries as a function of microfluidizer processing parameters.

Figure 2 shows the FE-SEM micrographs of the nanopaper surfaces with fibrous network structures. As the mechanical homogenization proceeds with fibrillation, more uniform surface morphology can be seen with finer fibrils and fibers. This result is consistent with the particle size analyses. Even though the particle size analyzer is not an absolute method to determine the fiber diameter and length, it can be used to provide relative values of fiber sizes. The lower magnification micrographs of W-5-45000-10 and A-5-45000-10 show the nonporous film but their higher magnification micrographs show the porous structures with swirled and entangled fiber networks. Nanofibril cellulose fibers are clearly manifest with the diameter below 50 nm, confirming that the fibril diameter was decreased to a nanoscale size by the homogenization process, and nanopapers were successfully prepared in this study.

The tensile test results for nanopapers are presented in Table 2, demonstrating that the strength and modulus increases with homogenization proceeding to the smaller nozzle size and higher operation pressures. The final nanopaper, e.g. W-5-45000-10, has about 8 times strength and modulus as larger as those of the virgin paper. The mechanical enhancement of the nanopaper can be explained by finer fiber structures and more extensive interfiber bonding with less porosity. However, the properties are less than the previous literature date [2] due to the dry process at ambient pressure. The application of pressure on nanopapers during drying may increase the mechanical properties because the extent of out-of-plane oriented fibers is reduced by the applied pressure and the increased in-plane fiber orientation can improve the mechanical properties.

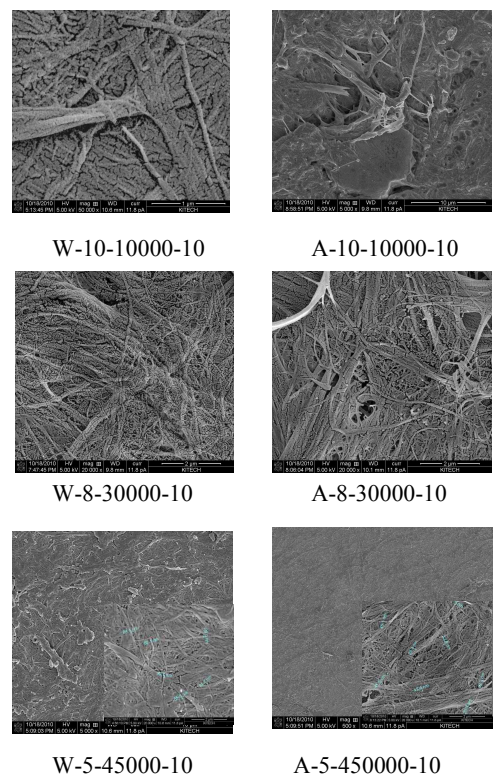


Figure 2: FE-SEM micrographs of nanopapers

Sample code	Strength [MPa]	Modulus [MPa]
Virgin	9.72	875.63
W-10-10000-10	20.35	2832.95
W-8-30000-10	52.59	4544.33
W-5-45000-10	92.06	5995.61
A-10-10000-10	27.34	3111.95
A-8-30000-10	72.87	5920.84
A-5-45000-10	-	-

Table 2: Tensile properties of nanopapers

The crystallinity index (CI) is the parameter to describe the relative amount of crystalline materials in cellulose [9]. The effects of processing conditions of the microfluidizer on CI show an increasing trend except for W-5-45000-10, as shown in Table 3. In the parallel nozzle setup, CI increases to 37.56% for W-8-30000-10 but then reduces to 24.02% for W-5-45000-10. However, the gradual increase was observed in the reverse nozzle setup. The increase in CI is explained by the previous evidence of the increase in CI by enzymatic hydrolysis due to the removal of the amorphous cellulose [9], and the decrease in CI can be attributed to damage to the pulp and nanofibers caused by the higher shear force in high pressure microfluidizer processes [10].

Table 3 shows a significant increase in specific surface area (SSA) of nanopapers, indicating the increased extent of fibrillation during homogenization progress. The final nanopapers such as W-5-45000-10 and A-5-45000-10 increase to the values of 226.23 and 282.15 m^2/g, respectively. The increase in SSA is in agreement to the results of the microscopic study, showing that the fiber diameter was reduced by a few orders of magnitude. The reduction in the fiber diameter can contribute to the higher SSA in the nanopaper. The higher SSA is an essential prerequisite for the reinforcements in nanocomposites. The nanoscale fibers with high SSA create one to three orders of magnitude more internal interfacial area per the fiber than the conventional microscale fibers [11]. The larger interfacial area with matrix materials improves the reinforcement efficiency by increasing the interfacial area to transfer stresses from the matrix materials to or between fibers.

Sample code	CI [%]	$[A]_{max}$ [mg/g]	SSA [m^2/g]
Virgin	22.98	82.21	128.9
W-10-10000-10	34.56	88.50	132.33
W-8-30000-10	37.58	109.89	164.33
W-5-45000-10	24.02	151.29	226.23
A-10-10000-10	24.36	98.04	146.60
A-8-30000-10	28.47	140.86	210.61
A-5-45000-10	30.59	188.68	282.15

Table 3: Crystallinity index of nanopapers

4 CONCLUSIONS

Cellulose nanofibers and their nanopaper were successfully prepared using high pressure homogenization processes with a microfluidizer and vacuum filtration paper-making processes, respectively. It was found that the homogenization process was effective to facilitate the fibrillation of cellulose into submicron and/or nanoscale nanofibers in pulp slurries, leading to the fiber diameter less than 50 nm. The increase in the tensile properties, crystallinity index and specific surface area of the nanopapers successfully demonstrated the potential use of cellulose nanofibers in the reinforcement for polymer nanocomposites.

REFERENCES

[1] R. Vaia, "Polymer nanocomposites open a new dimension for plastics and composites," AMPTIAC, 6, 17, 2002.

[2] M. Henriksson, L. Berlund, P. Isaksson, T. Lindstrom and T. Nishino, "Cellulose nanopaper structure of high toughness," Biomacomolecules, 9, 1579, 2008.

[3] M. Henriksson, G. Henriksson L. Berlund and T. Lindstrom, "An environmentally friendly method for enzyme-assisted preparation of microfibrillated cellulose (MFC) nanofibers," Eur. Polym. J., 43, 3434, 2007.

[4] www.beei.com.

[5] L. Mwaikambo and M. Ansell, "Chemical modification of hemp, sisal, jute, and kapok fibers by alkalization," J. Appl. Polym. Sci., 84, 2222, 2002.

[6] S. Lee, Y. Teramoto and T. Endo, "Enhancement of enzymatic accessibility by fibrillation of woody biomass using batch-type kneader with twin-screw elements," Bioresource Technol., 101, 769, 2010.

[7] F. Herrick, R. Caserbier, J. Hamilton and K. Sandberg, "Microfibrillated cellulose: morphology and accessibility," J. Appl. Polym. Sci., Appl. Polym Symo., 37, 797, 1983.

[8] A. Turbak, F. Snyder and K. Sandberg, "Microfibrillated cellulose, a new cellulose product: properties, uses, and commercial potential," J. Appl. Polym. Sci., Appl. Polym Symo., 37, 815, 1983.

[9] S. Park, J. Baker, M. Himmel, P. Prallia and D. Johnson, "Cellulose crystallinity index: measurement techniques and their impact on interpreting cellulose performance," Biotechnology for Biofuels, 3, 1, 2010.

[10] K. Uetani and and D. Yano, "Nanofibrillation of wood pulp using a high speed blender," Biomacromolecules, 12, 348, 2011.

[11] R. Vaia and and D. Wagner, "Framework for nanocomposites," Materials Today, 7, 32, 2004.