

# Novel Process for Isolating Fibrils from Cellulose Fibers by High-Intensity Ultrasonication. II. Fibril Characterization

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**ABSTRACT:** High-intensity ultrasonication with a batch process was used to isolate fibrils from several cellulose sources, and a mixture of microscale and nanoscale fibrils was obtained. The geometrical characteristics of the fibrils were investigated with polarized light microscopy, scanning electron microscopy, and atomic force microscopy. The results show that small fibrils with diameters ranging from about 30 nm to several micrometers were peeled from the fibers. Some fibrils were isolated from the fibers, whereas some were still on the fiber surfaces. The lengths of untreated and treated cellulose fibers were investigated by a fiber size analyzer. The

crystallinities of some cellulose fibers were evaluated by wide-angle X-ray diffraction and Fourier transform infrared spectroscopy. The high-intensity ultrasonication technique is an environmentally benign method and a simplified process that conducts fiber isolation and chemical modification simultaneously and helps significantly reduce the production cost of cellulose nanofibers and their composites. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 2756–2762, 2010

**Key words:** atomic force microscopy (AFM); biofibers; microstructure; separation techniques

## INTRODUCTION

The first article in this series presented a protocol of the isolation of cellulose fibrils from several cellulose fibers with high-intensity ultrasonication (HIUS) as an approach without any chemical treatment. A HIUS titanium tip was used to treat cellulose materials suspended in water with a batch process.<sup>1</sup> HIUS waves can produce a very strong mechanical oscillating power because of cavitation. The cavitation includes the formation, expansion, and implosion of microscopic gas bubbles when the molecules in a liquid absorb ultrasonic energy. Within the cavitation bubbles and the immediate surrounding area, violent shock waves are produced, which can be used to isolate fibrils from cellulose fibers.<sup>1,2</sup> In this study, we aimed to characterize the treated fibers, the separated fibrils, and the potential byproducts.

Many methods have been used for fibril characterization in the literature, including physical and chemical analyses and mechanical characterization. Several tools are available for morphological observation, including polarized light microscopy (PLM), scanning electron microscopy (SEM),<sup>3–5</sup> atomic force microscopy (AFM),<sup>5–7</sup> and transmission electron microscopy (TEM).<sup>3,8</sup> PLM is used to observe relative materials of large dimension, above micrometers, whereas AFM, SEM, and TEM can be used to observe much materials of smaller dimension, below micrometers to nanometers. Wide-angle X-ray diffraction (WAXD) has been used to study the crystallinity of cellulose fibrils.<sup>4</sup> The estimated crystallinity of nanofibers from wood kraft pulp was 54%, whereas the crystallinity values of flax and rutabaga nanofibers were estimated at 59 and 64%, respectively.<sup>9</sup> The chemical properties of chemically treated cellulose fibers have been studied by Fourier transform infrared (FTIR) spectroscopy.<sup>9</sup> Some ratios of peak absorbance to the nearby valley in FTIR spectra can be used to compare cellulose crystallinities because the chemical structure of amorphous and crystalline cellulose are identical and different in the physical environment of the bonds, which will give FTIR spectra with slightly different characteristics.<sup>10,11</sup> The surface charge of fibrils has been measured by conductometric titrations with sodium

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**TABLE I**  
**Summary of the Dimensional Analyses of the Fibers and Fibrils Measured with a Kajaani FiberLab 3 Fiber Size Analyzer**

Fiber	Sample	Continuous length weighted average (mm) <sup>c</sup>	Continuous length weighted average (mm) <sup>d</sup>	Continuous fines (%) <sup>e</sup>	Width (μm)	Curl (%)	Cross-sectional area (μm <sup>2</sup> )
Lyocell	Raw fiber	0.97	1.04	8.06	16.4	10.0	160
Lyocell	Mixture <sup>a</sup>	0.87	0.95	10.29	17.7	11.2	201
Lyocell	Separated fibrils <sup>b</sup>	0.27	0.53	67.99	13.1	4.9	174
TC180	Raw fiber	0.26	0.42	62.56	12.5	5.9	166
TC180	Mixture <sup>a</sup>	0.23	0.42	67.66	11.6	4.5	156
TC180	Separated fibrils <sup>b</sup>	0.17	0.56	87.96	8.2	2.8	133

<sup>a</sup> After HIUS for 30 min.

<sup>b</sup> After centrifugation for 5 min (HIUS for 30 min).

<sup>c</sup> 0.25–7.60 mm.

<sup>d</sup> 0.00–7.60 mm.

<sup>e</sup> 0.00–0.25 mm.

hydroxide.<sup>7</sup> The mechanical properties of a single cellulose fibril are very important, especially when the ultimate purpose of the fibrils is the reinforcement of composite materials. The elastic moduli of bacterial cellulose nanofibers and Lyocell fibrils have been measured with AFM.<sup>5,12</sup>

In this study, the geometric characteristics of treated and separated fibrils by HIUS were investigated with PLM, SEM, and AFM. Energy-dispersive X-ray spectrometry (EDS) and FTIR were used to check the possible byproducts of ultrasonic treatment. The crystallinities of the treated and untreated cellulose fibers were studied by WAXD and FTIR.

## EXPERIMENTAL

### Materials

Four different cellulose sources from regenerated cellulose fiber (Lyocell, Lenzing, Austria) and original cellulose were used as raw materials. The three original cellulose materials with different sizes were TC180 (pure cellulose fiber, CreaFill Fibers Corp., Chestertown, MD), Avicel (microcrystalline cellulose, PH-101, FMC BioPolymer, Philadelphia, PA), and pulp fiber (Kimberly-Clark Worldwide, Inc., Draper, UT). Microfibrillated cellulose (10% solid slurry, Dai-Cell Chemical Industries, Ltd., Japan) was used as a reference. The fibrils were isolated from these cellulose fibers with HIUS.<sup>1</sup>

### Characterization of the potential byproducts

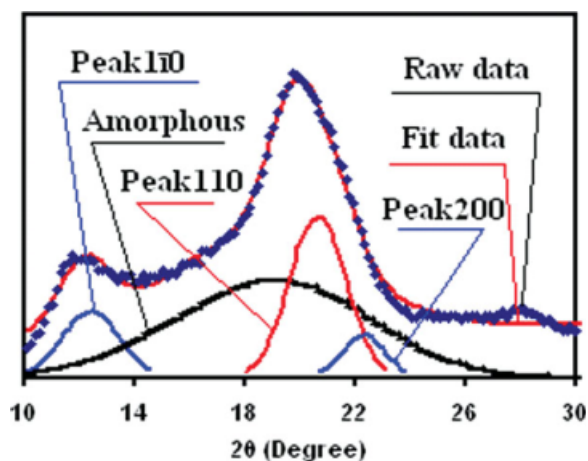
SEM (LEO 1525, Peabody, MA) with an Oxford energy dispersive X-ray spectrometer was used to check the black particles obtained during HIUS treatment. EDS, a chemical microanalysis technique, was performed in conjunction with SEM.

FTIR (PerkinElmer molecular spectroscope, Spectrum One, Waltham, MA) with an attenuated total

reflectance (ATR) accessory was used to obtain the spectra for fibers before and after treatment. FTIR samples were from the materials used for water retention value (WRV) measurements.<sup>1,4</sup> Some Lyocell samples were prepared by the drying of a treated fiber suspension on aluminum foil. Water samples from the top of centrifuged suspensions were scanned by FTIR to check for some soluble content in the suspensions of treated fibers. Midinfrared spectra were recorded in the wave-number range 4000–600 cm<sup>-1</sup>. These spectra were taken at a resolution of 4 cm<sup>-1</sup> with a total of 16 scans for each sample. To compare different spectra, all of the water spectra were normalized on the peak at 3322 cm<sup>-1</sup>. The fiber spectra were normalized on the peak at about 1019 cm<sup>-1</sup> attributed to a CO stretching mode.<sup>10</sup> Then, all the spectra were corrected by attenuated total reflectance (ATR). After normalization and ATR correction, two ratios of peak absorbance to the nearby valley, which could be used to compare the cellulose crystallinities, 1156/1141 and 1419/1405 cm<sup>-1</sup> for Lyocell fiber and 1105/1087 and 1429/1397 cm<sup>-1</sup> for Avicel and TC180, respectively, were compared to estimate the changes between the treated and untreated cellulose fibers due to the differences in the chemical structures of the amorphous and crystalline cellulose in the FTIR spectra.<sup>11</sup>

### Dimensional analyses of the fibers and fibrils

A fiber size analyzer (Kajaani FiberLab 3, Metso, Automation, Finland) was used to analyze the dimensions of the untreated and treated cellulose fibrils (Lyocell and TC180). Three samples [raw fiber (untreated fiber soaked in water for more than 48 h), mixture (treated for 30 min), and separated fibrils] were prepared for each analysis (Table I). The Kajaani fiber length (continuous length weighted average = 0.25–7.60 and 0.00–7.60 mm), fine fiber length (0.00–0.25 mm), average fiber width, cross-

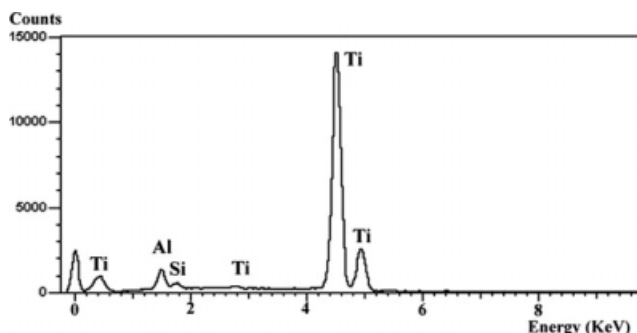


**Figure 1** Typical Lyocell fiber WAXD curves with amorphous and three major crystalline peaks. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

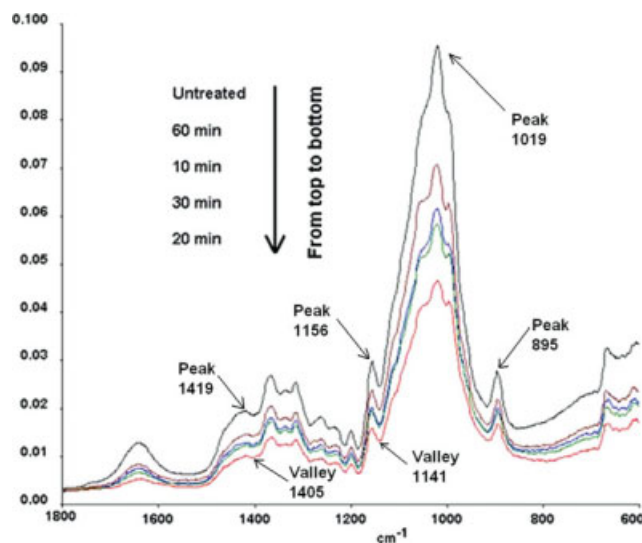
sectional area ( $\mu\text{m}^2$ ), and Kajaani percentage curl [a mathematical function of the continuous fiber length (which measures the fibers pixel to pixel along the center line of the fiber) to the projected fiber length (with the curves and bends in the fiber not taken into account)] were measured. Each sample was analyzed in triplicate. The continuous fiber length distributions were also analyzed.

### Cellulose crystallinity measurements

The crystallinities of the treated and untreated Lyocell fibers were studied with WAXD (Molecular Metrology Inc., Northampton, MA).<sup>4,13</sup> Reflection-integrated intensities were determined by deconvolution of the diffraction peaks into a series of peaks by PeakFit v4.12 software (SYSTAT, Chicago, IL). The crystallinity was estimated from the peak areas of the (110), (110), and (200) planes, which had  $2\theta$  values of 12, 20, and 22°, respectively. The percentage crystallinity was calculated from the relative areas of the amorphous and three major crystalline peaks (Fig. 1).<sup>14</sup>



**Figure 2** Elemental compositions of the black particles analyzed with EDS.

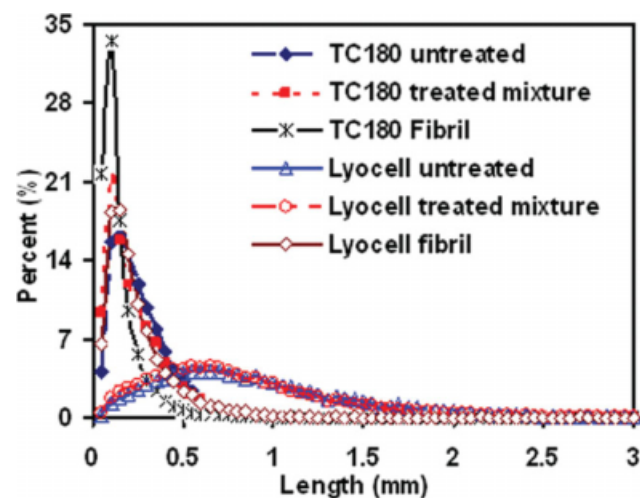


**Figure 3** Mid-FTIR spectra of untreated and treated Lyocell fibers between 1800 and 600  $\text{cm}^{-1}$ . [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

FTIR was also used to obtain the spectra to estimate the crystallinities of the treated and untreated cellulose fibers. The cellulose IR crystallinity index was evaluated as the intensity ratio between the IR absorptions at 1419 and 895  $\text{cm}^{-1}$  for the Lyocell fiber and those at 1429 and 898  $\text{cm}^{-1}$  for Avicel and TC180, which were attributed to the  $\text{CH}_2$  bending mode and deformation of anomeric  $\text{CH}$ , respectively.<sup>10</sup> At least three samples were scanned for each cellulose source.

### Morphology observations

The appearances and dimensions of the treated and untreated cellulose fibers were studied with PLM



**Figure 4** Continuous fiber length distributions of TC180 and Lyocell. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

TABLE II  
Lyocell Sample Crystallinities Estimated by WAXD and FTIR

Treatment time (min)	0	10	20	30
WAXD peak area ratio method (%)	35	44	43	44
FTIR peak ratio (1419/895): dry samples	0.62 (0.02)	0.60 (0.01)	0.63 (0.02)	0.63 (0.02)
FTIR peak ratio (1419/895): WRV samples	0.65 (0.05)	0.65 (0.02)	0.61 (0.02)	0.66 (0.04)

The numbers in parentheses are the standard deviations.

(BX51, Olympus). Some fibers and fibrils were measured from the pixels in the images with the software package ImageJ.<sup>4</sup> The morphology of the separated fibrils was also examined with SEM (LEO 1525) and AFM (PSIA, XE-100, Suwon, Korea). A drop of fibril suspension was dried on a silicon wafer and then scanned by SEM or AFM. The operating voltages of SEM ranged from 5 to 10 kV, and various magnification levels were used to obtain the images. AFM scanning was performed with contact or noncontact mode with a sharp tip with a radius of less than 10 nm (ZEILR, Nanosensor, Neuchatel, Switzerland).

## RESULTS AND DISCUSSION

### Characterization of the black particles

During the process, some black particles were formed, which were proven by EDS to be titanium from the tip of the ultrasonic processor (Fig. 2). This demonstrated that the cellulose was not oxidized and degraded to carbon. When the treatment time was more than 30 continuous minutes or the tip was used too many times, black particles of diameter 2  $\mu\text{m}$  or less could be observed in the suspension. This indicated that a new tip material with less erosion was helpful for cellulose fibril isolation.

### FTIR analysis of the treated fibers and water

No significant differences among distilled water, water from treated Avicel suspensions, and water from Lyocell cellulose were detected in the mid-FTIR spectra. This indicated that no soluble components were observed in the suspensions after the cellulose materials were treated by HIUS.

Some peak changes related to  $\text{CH}_2$  bending were observed for the Lyocell fibers treated by HIUS (Fig. 3). The ratio of  $1419/1405\text{ cm}^{-1}$  was significantly different between the WRV samples and the samples dried on aluminum foil. There were no significant differences for the ratio of  $1156/1141\text{ cm}^{-1}$  between the two samples, except at the 10-min treatment. This demonstrated that they had different cellulose crystallinities.<sup>10,14</sup> This may have been because the WRV samples had fewer small fibrils due to filtration by a membrane with  $0.2\text{-}\mu\text{m}$  holes.<sup>4</sup>

Both ratios of Avicel cellulose ( $1105/1087$  and  $1429/1397\text{ cm}^{-1}$ ) significantly decreased after the treatment, and significant differences were detected among the three treatments (10, 20, and 30 min). This indicated that these samples had different cellulose crystallinities, so HIUS treatment changed the Avicel molecular structure. For TC180, the two ratios had few differences before and after treatment.

### Dimensional analyses of the fibers and fibrils

The average width of the water-soaked untreated Lyocell ( $16.4\text{ }\mu\text{m}$ ) was higher than the original width of the dry fiber ( $11\text{ }\mu\text{m}$ ) because it swelled on soaking in water (Table I). The average width of the treated Lyocell ( $17.7\text{ }\mu\text{m}$ ) was higher than that of the untreated Lyocell, which indicated that the fibers were getting loose, some small fibrils were on the surfaces of big fibers, and big fibers still dominated the treated Lyocell fibers. For TC180, the average width before treatment ( $12.5\text{ }\mu\text{m}$ ) was much smaller than the original width of the dry fiber ( $20\text{ }\mu\text{m}$ ) because the fiber analyzer used a camera to measure the widths of fibers suspended in water and passed the lens of the camera and the original fibers had a very small thickness ( $1\text{--}2\text{ }\mu\text{m}$ ). The continuous fiber length distributions of the two materials, both before and after treatment, and the

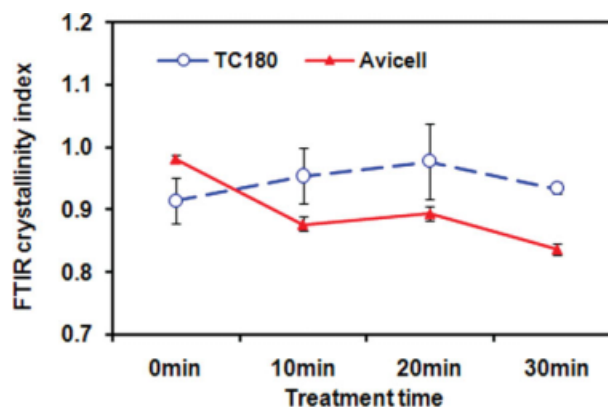
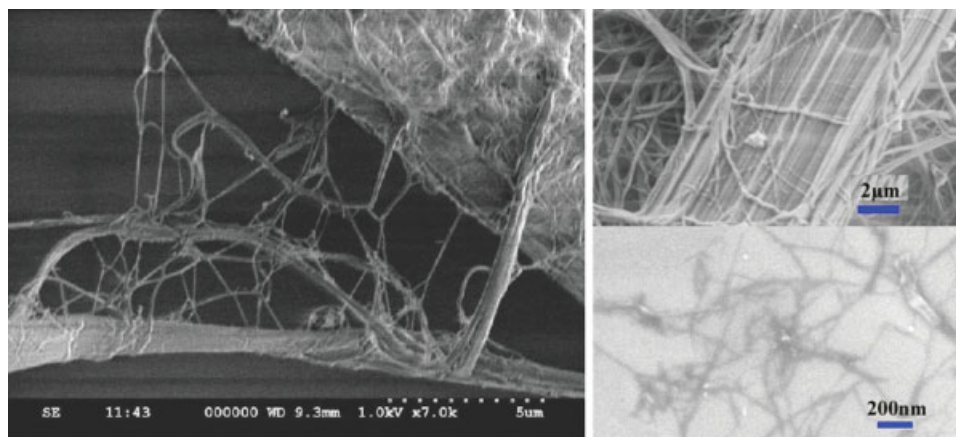


Figure 5 FTIR crystallinity indices of TC180 and Avicel for different treatment times. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 6** SEM images of Lyocell fibers and fibrils. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

separated fibrils indicated that there were more short components in the treated materials and separated fibrils (Fig. 4).

#### Crystallinity changes

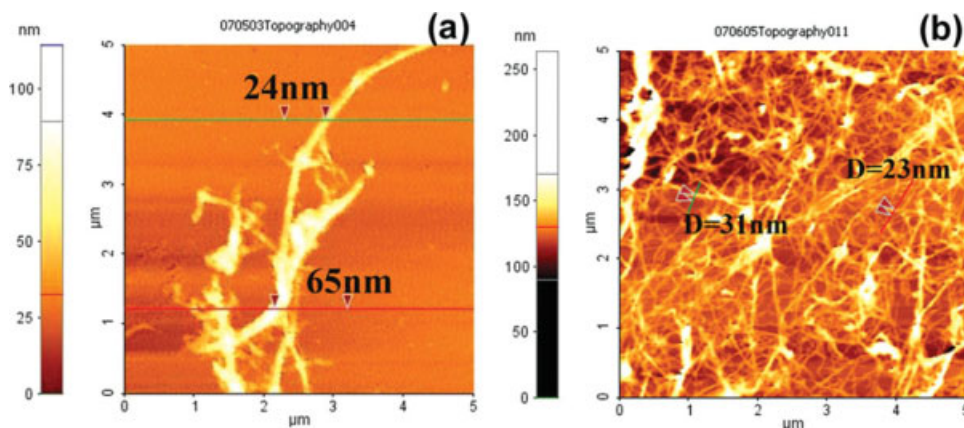
The crystallinity measurement of the treated samples was important because the ultrasonic treatment of cellulose caused a strong decrease in the degree of polymerization.<sup>15</sup> The crystallinity of the treated Lyocell fibers increased as the treatment time exceeded that estimated by WAXD. All four cellulose samples had a narrow peak at a  $2\theta$  of about  $20^\circ$  and a lower peak at a  $2\theta$  of about  $12^\circ$  (Fig. 1). The crystallinities of the untreated (35%) and treated (43–44%) Lyocell fibers were calculated from the X-ray diffraction patterns with the area ratio method. The results were much lower than those estimated by the Segal method but had a similar increasing trend.<sup>4</sup> The cellulose crystallinities can be affected dramatically by different calculation methods

because of the overlapping and widely broadened diffraction peaks of cellulose.<sup>13</sup> The crystallinity indices of the Lyocell fibers were also evaluated by FTIR. Unlike the WAXD results, the crystallinity of the treated Lyocell fibers was not increased much. The crystallinity data obtained by both the WAXD and FTIR methods for the Lyocell samples are summarized in Table II.

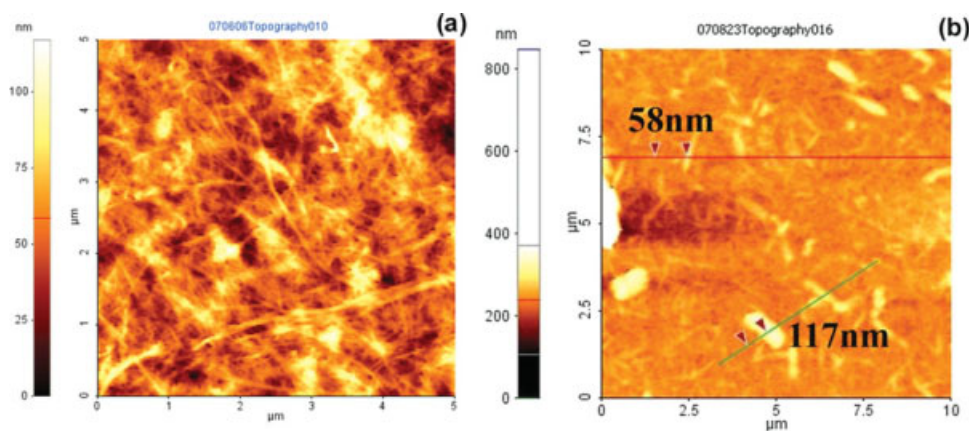
The crystallinity indices of TC180 and Avicel were evaluated by FTIR (Fig. 5). HIUS treatment significantly decreased the FTIR crystallinity index of the Avicel fibers, presumably because Avicel had a relatively high crystallinity and HIUS treatment changed some crystal structure of the Avicel cellulose.<sup>10,14,16</sup> For TC180, HIUS treatment did not change the FTIR crystallinity index.

#### Morphological analysis of the fibers and fibrils

After a 30-min treatment, a mixture suspension of fibers and fibrils with diameters ranging from



**Figure 7** AFM topography images of (a) Lyocell and (b) TC180 fibrils. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 8** AFM topography images of (a) pulp and (b) Avicel fibrils. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

micrometers to 10s of nanometers was obtained. Many small fibrils with diameters less than 1  $\mu\text{m}$  were peeled from the Lyocell fibers. Some fibrils were still on the surfaces of the big ones that dominated the treated fibers, whereas some were already isolated from the big fibers (Fig. 6). The diameters or widths of the fibrils isolated from the Lyocell fibers were in the range of 10s to 100s of nanometers and had a wide range of aspect ratio (length/diameter). The AFM images of fibrils showed some small fibrils with diameters of 20–30 nm [Fig. 7(a)]. Compared with commercial microfibrillated cellulose, the fibrils generated by HIUS after a 30-min treatment and separated by a centrifuge had a similar range of diameters from 10s of nanometers to several micrometers.

Smaller fibrils isolated from TC180 with diameters around 20–30 nm were also observed, and the aspect ratios of the fibrils were much bigger than the untreated cellulose [Fig. 7(b)], which is helpful for polymer reinforcement.<sup>6</sup> Most fibrils separated from pulp fibers in the top-portion suspension in a tube after centrifugation were on the micrometer scale or less. Some small fibrils were observed after a 90-min HIUS treatment [Fig. 8(a)].

The aspect ratio of the untreated Avicel cellulose was small. After HIUS treatment, most particles were split into smaller fibrils [Fig. 8(b)]. This was why a very stable suspension was obtained after the 30-min treatment. Most fibrils were several 100s of nanometers, and some of them were around 100 nm or less. The aspect ratios of the fibrils were much bigger than those of the untreated cellulose, which helped to reinforce the polymers.<sup>4,6</sup>

## CONCLUSIONS

After HIUS treatment, a mixture of microscale and nanoscale fibrils was obtained from Lyocell, TC180,

and Avicel celluloses. Some fibrils were still on the surfaces of the big ones, whereas some others were isolated from the fibers. Black titanium particles were found in the cellulose suspensions when the ultrasonic tip was used for too long a time. The length and width of the treated cellulose fibers were found to be significantly decreased on evaluation by the fiber analyzer. The observations of PLM, SEM, and AFM showed that the size of the fibrils had a wide diameter ranging from about 20–30 nm to several micrometers. The cellulose crystallinity structure of some cellulose fibers was changed by ultrasonic treatment, and the changes were different for different cellulose sources; that is, it increased for Lyocell, decreased for Avicel, and stayed the same for pulp fiber. HIUS could be used to isolate fibrils from cellulose fibers, which can be used to reinforce polymers to make biodegradable composites. A potential application of this research is that waste cellulose, such as waste Lyocell fabrics and waste papers, may be used as raw materials to separate high-value cellulose fibrils.

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## References

1. Wang, S.; Cheng, Q. *J Appl Polym Sci* 2009, 113, 1270.
2. Suslick, K. S. *Science* 1990, 247, 1439.
3. Choi, Y. J.; Simonsen, J. *J Nanosci Nanotechnol* 2006, 3, 633.
4. Cheng, Q.; Wang, S.; Rials, T. G.; Lee, S. H. *Cellulose* 2007, 6, 593.
5. Cheng, Q.; Wang, S. *Compos A* 2008, 39, 1838.
6. Cheng, Q.; Wang, S.; Rials, T. G. *Compos A* 2009, 40, 218.
7. Beck-Candanedo, S.; Roman, M.; Gray, D. G. *Biomacromolecules* 2005, 2, 1048.

8. Zimmermann, T.; Pohler, E.; Geiger, T. *Adv Eng Mater* 2004, 9, 754.
9. Bhatnagar, A.; Sain, M. *J Reinforced Plast Compos* 2005, 12, 1259.
10. Kataoka, Y.; Kondo, T. *Macromolecules* 1998, 3, 760.
11. Schultz, T. P.; McGinnis, G. D.; Bertran, M. S. *J Wood Chem Technol* 1985, 4, 543.
12. Wan, W. K.; Hutter, J. L.; Millon, L.; Guhadós, G. *Cellulose Nanocomposites: Processing, Characterization, and Properties*; ACS Symposium Series; American Chemical Society: Washington, DC, 2006; Volume 938, p 221.
13. Thygesen, A.; Oddershede, J.; Lilholt, H.; Thomsen, A. B.; Stahl, K. *Cellulose* 2005, 6, 563.
14. Kaplan, D. L. *Biopolymers from Renewable Resources*; Springer-Verlag: Berlin, 1998; p 55.
15. Marxfigini, M. *Angew Makromol Chem* 1997, 250, 85.
16. Zheng, Y. Z.; Lin, H. M.; Wen, J. Q.; Cao, N. J.; Yu, X. Z.; Tsao, G. T. *Biotechnol Lett* 1995, 17, 845.