Oxidized Fiber from Dissolved Air Flotation Rejects and its Influences on Paper Properties

Yanghong Wang, and Xianliang Song*

Fibers obtained from dissolved air flotation rejects were oxidized using a TEMPO oxidation system to prepare oxidized recovered fibers. The effects of oxidization time on carboxyl content, water retention value, and physical properties of handsheets were evaluated. The effects of pH, amount of oxidized recovered fibers, and aluminum sulfate on paper properties were also considered. The results showed that carboxyl content and water retention values increased with the increasing of oxidized time. FTIR analysis indicated that carboxyl groups were connected to the surface of fibers. SEM micrographs showed that fibers were integrated more closely in the paper sheet, benefiting from the addition of the oxidized recovered fibers. Tensile index, burst index, and folding endurance were respectively increased by 71.7%, 38.5%, and 600% when 3% of oxidized recovered fibers was added to the pulp at pH 5, with 0.5% aluminum sulfate addition, based on the original pulp. Tensile index and folding endurance were increased by 40.2% and 433.3%, respectively, when 1% oxidized recovered fibers (the oxidized time was 60 min) were added into pulp for recycled pulp. This finding may lay the foundation for greater re-use of fiber obtained from dissolved air flotation rejects.

Keywords: Fiber; Dissolved air flotation rejects; Oxidation

*Contact information: College of Material Science and Technology, Beijing Forestry University, Beijing, 100083, China; *Corresponding author: sxlswd@163.com*

INTRODUCTION

Pulp consumption in China has reached 90.44 million tons, while pulp production was 77.23 million tons in 2011 according to annual reports of China's paper industry (China Technical Association of Paper Industry 2009; China Technical Association of Paper Industry 2011). With increasing demand for paper and a shortage of fibrous material in China, recycled paper has received great attention in the past few years. Deinking is an important process in paper recycling. Flotation tanks are used for removing ink particles and impurities of the recycled pulp during the manufacture of paper. Large quantities of rejects from dissolved air flotation coming from the flotation deinking process are discarded or buried, which can cause environmental contamination. Between 10% and 20% of the fibers in the dissolved air flotation rejects are also lost (Chaiarrekij *et al*. 2000; Ben *et al*. 2004, 2006; Chen *et al*. 2012). It would be helpful for environmental protection and saving of raw material if the lost fibers were instead prepared for use in high value-added products.

TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy)-mediated oxidation has often been used in recent years to convert the C_6 hydroxyls of carbohydrates into carboxyl groups, which can be utilized to improve the properties of handsheets by increasing the anionic charge on the fiber surface (Song and Law 2010).

This study was aimed at recycling the fiber content of dissolved air flotation rejects. Fibers obtained from dissolved air flotation rejects were oxidized to obtain oxidized recovered fibers. Then the oxidized recovered fibers were added into kraft pulp of triploid *Populus tomentosa* Carr. The influence of oxidatized fibers from dissolved air flotation rejects on handsheet physical properties was studied.

EXPERIMENTAL

Materials

Dissolved air flotation rejects were obtained from the production line of waste paper deinking of No. 7 paper mill of Beijing. Its moisture content was 75.22%. The kraft pulp of triploid *Populus tomentosa* was prepared under laboratory conditions, which were: liquor ratio 1:4.5, alkali dosage 16%, sulfidity 25%, maximum temperature 165 °C, heating time 2 h, soaking time 2 h, and beating degree 40 ° SR.

Methods

Collection of fibers from dissolved air flotation rejects

Dissolved air flotation rejects, 150 g (wet weight), were mixed with 10 L of distilled water and then screened using a 100-mesh sieve. The fiber above 100 mesh size was then washed clean and kept in cold storage.

TEMPO oxidization

Fifteen grams of the collected fibers and 1500 mL distilled water were combined in a 2000 mL 3-neck flask equipped with a stirring apparatus. The flask was then put in a water bath at 21 °C, where 0.0713 g of TEMPO, 9.5378 g of sodium bromide, and 2.6 mL of sodium hypochlorite solution (> 9% concentration w/w) were then added in the flask, still with stirring. The pH value of the system was adjusted to about 10.5 with 0.4 mol/L hydroxide solution. Next, the timing was started. Five minutes later, another 2.6 mL of sodium hypochlorite solution was added to the flask. The pH value of the system was adjusted to about 10.5. Another 5 minutes later, 1 mL of sodium hypochlorite solution was added in the flask. Still the pH value of the system was adjusted to about 10.5. The mixture was respectively oxidized for 20 min, 30 min, 40 min, and 60 min, and washed 2 to 3 times with distilled water. Then four samples of oxidized recovered fibers were obtained (Song and Law 2010).

Cationization

Sodium hydroxide, in the amount of 0.065 g, and 26 g of collected fibers (moisture content: 75.22%) were put into a 100 mL beaker flask with an impeller stirring apparatus. The mixture was stirred at room temperature until the sodium hydroxide was dissolved. Then 3-chloro-2-hydroxypropyl–trimethyl ammonium chloride (10%, 20%, 30%, or 50% of fiber dry basis) was put into the beaker flask, the mixture was stirred for 10 min, the beaker flask was put into the 70 °C stove for 4 h, then 60 mL distilled water was combined in the beaker flask, The mixture was filtered off by filter paper, washed four times with 100 mL distilled water, and dried in air. In this manner four samples of cationic recovered fibers were obtained.

Carboxyl content

Carboxyl content was determined by a conductiometric titration technique (Katz *et al*. 1984).

Papermaking and physical properties of paper sheets

Standard paper sheets of 60 g/m^2 were prepared and tested in accordance with the China GB standard methods. Other papermaking conditions were as follows: 0.5% $Al_2(SO4)_3$, pH as given. A portion of the paper samples were immersed in water at room temperature for 24 h, then disintegrated and without further addition of chemicals, the pulp samples were formed again into recycled handsheets in accordance with China GB standard methods (Wang *et al*. 2012).

Papermaking with both TEMPO oxidized fibers and cationic fibers

0.5% TEMPO oxidized fibers (TOF) and 0.5% cationic fibers (CF) were mixed and added into kraft pulp of triploid *Populus tomentosa.*

Standard paper sheets of 60 g/m^2 were prepared and tested in accordance with the China GB standard methods. Other papermaking conditions were as follows: 0.5% $Al_2(SO_4)_3$, pH as given.

SEM

S-3000N SEM was used for observation of the paper surfaces and fracture surfaces.

Atomic force microscope (AFM)

The oxidized recovered fibers were characterized using a Shimadzu SPn9000 Scanning probe microscope. Images were collected using a phase mode with a constant force. A droplet of the 1% oxidized recovered fibers suspension was dried on a mica surface prior to AFM testing. Then they were analyzed directly.

Measurement of water retention value (WRV)

Determination of the WRV value of the samples was carried out using a centrifuge LD4-2-A (Beijing Medical Factory, China). The speed used was 3000 rev/min, and the time was 15 min. About 1 g sample pulp (o.d. basis) was diluted in 60 mL deionized water overnight at room temperature. Then the pulp was put into a copper tube with a 200-mesh copper screen at the bottom. Other details were given in a previous work of ours (Law *et al*. 2006).

RESULTS AND DISCUSSION

Effects of Oxidized Time on Carboxyl Content

Effects of oxidization reaction time on carboxyl content are presented in Fig. 1. As shown in Fig. 1, the carboxyl content increased with increasing of oxidized reaction time. The carboxyl content increased from 28.3 mmol/kg to 87.6 mmol/kg when the oxidation reaction time was increased from 20 min to 60 min.

Effects of Carboxyl Content on Water Retention Value

Effects of carboxyl content on water retention value are presented in Fig. 2. As shown, the water retention value increased with increasing of carboxyl content. The water retention value increased from 83.4 g/100 g to 95.8 g/100 g when the carboxyl content increased from 28.3 mmol/kg to 87.6 mmol/kg. This indicates that the carboxyl groups adsorbed a certain amount of water, thus reducing the hydrophobicity.

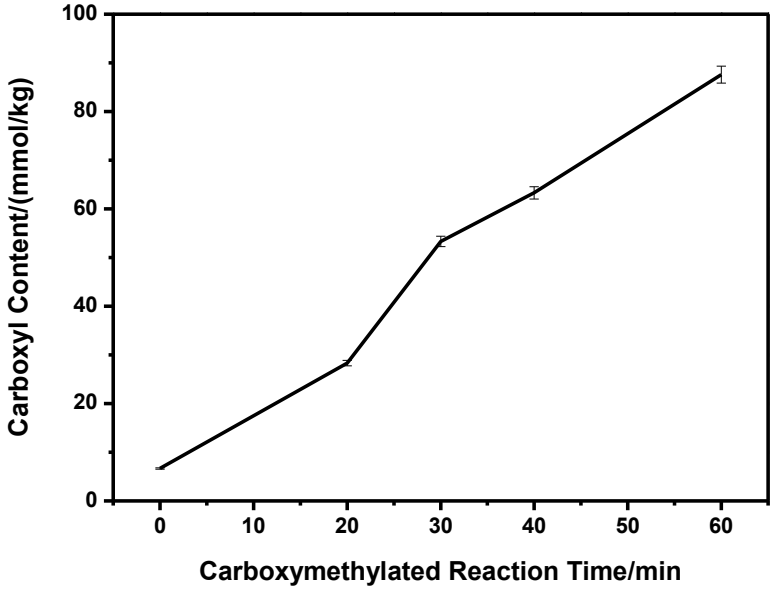

Fig. 1. Effects of oxidized reaction time on carboxyl content

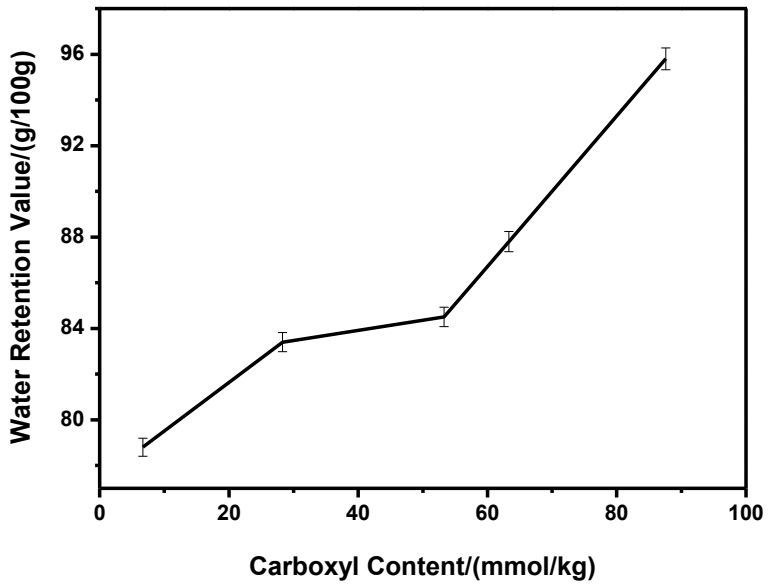

Fig. 2. Effects of carboxyl content on water retention value

Effects of Oxidized Time on Handsheet Properties

As shown in Table 1, tensile index, burst index, and folding endurance increased with increasing oxidized time, while tear index showed an opposite trend.

Table 1. Effects of Oxidized Time on Handsheet Properties

Oxidized time (min)	Tensile Index (Nm/g)	Tear Index (mNm^2/g)	Burst Index ($kPam^2/g$)	Folding Endurance (double folds)
control	41.92	10.15	3.464	9
20	55.99	8.48	3.561	38
30	56.85	7.57	3.649	45
40	57.85	7.11	3.684	46
60	58.78	6.65	3.826	48

Note: Control sample is kraft pulp handsheet. 1% oxidized recovered fibers are added in the other four samples. The standard deviation is <4%

When the oxidized time was increased, carboxyl content increased gradually. The free carboxyl content and the number of hydrogen bonds also increased, which then increased the intensity of bonding within the handsheets. Tensile index and folding endurance increased by 40.2% and 433.3%, respectively when the oxidized time was 60 min. The fact that such large effects were observed even with only 1% of oxidized fiber material in the sheet is tentatively attributed to the presence of nanomaterials. As shown by Atomic Force micrographs (see Appendix), the nanofiber dimensions in the mixture treated by TEMPO oxidation were 100 to 200 nm in length, 20 nm in width, and height about 0.64 to 8.4 nm. Related effects due to the presence of nanomaterials were observed by Ioelovich and Figovsky (2010).

As shown in Table 2, tensile index, burst index, and folding endurance increased at first and then decreased with increasing content of oxidized fibers, while tear index showed a divergent trend. When the dosage of oxidized recovered fibers was less than 3%, the carboxyl content increased gradually. The free carboxyl content and the number of hydrogen bonds can be expected to follow a similar trend, which would increase the intensity of bonding within the paper sheets (Hubbe *et al*. 2003; Zhang *et al*. 2004; Zhu *et al*. 2011). When the dosage of oxidized recovered fibers amount exceeded 3%, the physical properties of paper sheets became worse, probably because of the increasing of negative charge, which would increase the repulsive force among the fibers. Tensile index, burst index, and folding endurance increased by 71.7%, 38.5%, and 600%, respectively, when the dose of oxidized recovered fibers was 3%.

Table 2. Effects of Dosage of Oxidized Recovered Fibers on Handsheet Properties

Dosage (%)	Tensile Index (Nm/g)	Tear Index (mNm^2/g)	Burst Index ($kPam^2/g$)	Folding Endurance (double folds)
control	41.92	10.15	3.464	9
1	58.78	6.65	3.826	48
2	66.81	6.74	4.572	54
3	71.97	6.79	4.798	63
4	60.62	7.00	4.759	34
5	61.45	7.14	4.898	32

Notes: Oxidized recovered fibers in this experiment was the sample that had been oxidized for 60 min. The standard deviation is <4%

Effects of pH on Handsheet Properties

As is shown in Table 3, tensile index, burst index, and folding endurance decreased gradually with the increasing of pH values. Al^{3+} was the dominant form in the pulp in the range between pH of 4 and 5. Al^{3+} is a highly cationic ion that has a very strong ability of form stable complexes with any dissociated carboxyl groups it comes into contact with. The initial complex helps to neutralize any excess anionic charge in the pulp and tie any alum floc onto the surfaces of fines and fibers, which will improve the strength of paper sheets.

Table 3. Effects of pH on Handsheet Properties

pH Values	Tensile Index (Nm/g)	Tear Index (mNm^2/g)	Burst Index ($kPam^2/g$)	Folding Endurance (double folds)
5	58.78	6.65	3.826	48
7	51.98	7.11	3.738	22
9	41.80	7.58	3.070	8

Notes: The standard deviation is <4%

Effects of Dosage of Aluminum Sulfate on Handsheet Properties

The effects of aluminum sulfate addition on properties of paper sheets are presented in Table 4. As shown, when the dose of aluminum sulfate was 0.5%, the handsheets exhibited the most favorable properties in terms of tensile, burst, and folding endurance. The reason for this was represented in the previous section.

Table 4. Effects of Dosage of Aluminum Sulfate on Handsheet Properties

Aluminum sulfate (%)	Tensile Index (Nm/g)	Tear Index (mNm^2/g)	Burst Index ($kPam^2/g$)	Folding Endurance (double folds)
0.25	57.23	6.69	4.321	51
0.5	58.78	6.65	3.826	48
0.75	47.12	7.44	3.742	28

Notes: The standard deviation is <4%

Handsheet Properties with Mixture of TOF and CF

As shown in Table 5, the tensile strength, bursting strength, and folding endurance of paper sheets with mixture of TOF and CF increased by 2.8%, 4.6%, and 46.8%, respectively, compared with paper sheets with only TOF. One can see that the use of a mixture of TOF and CF could be a better way to improve the physical properties of paper sheets.

Table 5. Handsheet Properties with Mixture of TOF and CF

Kinds and volume of modified fibers	Tensile Index (Nm/g)	Tear Index (mNm^2/g)	Burst Index ($kPam^2/g$)	Folding Endurance (double folds)
Control	41.92	10.15	3.464	9
1%TOF	58.78	6.65	3.826	48
0.5% TOF and 0.5%CF	60.42	6.44	4.003	70

Notes: The standard deviation is <4%

SEM

SEM fracture images of paper samples prepared without and with oxidized recovered fibers are presented in Figs. 3a and 3b. As shown in Fig. 3a, the majority of fibers were intact, while most fibers in Fig. 3b were fractured. SEM surface images of a paper sample without and with oxidized recovered fibers are presented in Fig. 3c and 3d, respectively. As is shown, there were more pores in Fig. 3c compared to Fig. 3d. This is because the oxidized recovered fibers increase the bonding force among fibers.

Effects of Oxidized Time on Physical Properties of Recycled Paper

The effects of oxidized time on physical properties of recycled paper are presented in Table 6.

Table 6. Effects of Oxidized Time on Physical Properties of Recycled Paper

Oxidized time (min)	Tensile Index (Nm/g)	Tear Index (mNm^2/g)	Burst Index ($kPam^2/g$)	Folding Endurance (double folds)
Control sample	17.91	6.136	1.558	3
20	29.78	5.414	1.933	5
30	34.59	5.305	2.203	8
40	33.55	5.441	1.788	7
60	32.34	5.434	1.708	6

Notes: The standard deviation is <5%

As can be seen, the tensile index, burst index, and folding endurance increased with the increasing of oxidized time. Tensile index and burst index, respectively, increased by 93.1 % and 41.4%. It is thus clear that the oxidized recovered fibers also can be effective for the production of recycled paper (Weise 1998; Hubbe *et al*. 2007).

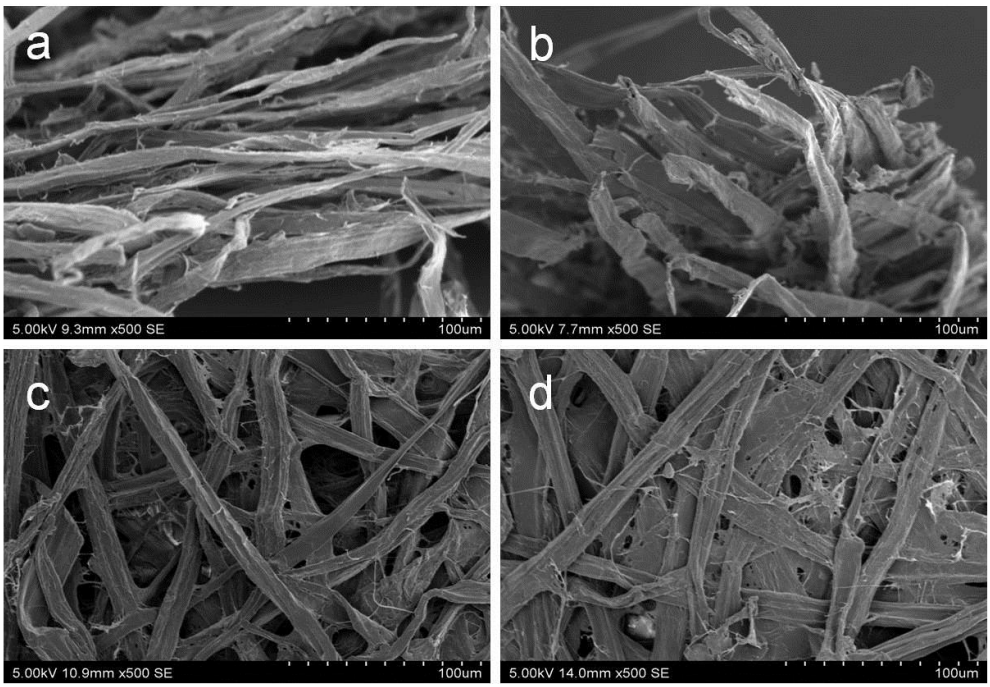

Fig. 3. SEM fracture surface images and surface images of a paper sample: (a) control, (b) with oxidized recovered fibers, (c) control, and (d) with oxidized recovered fibers

CONCLUSIONS

The following main conclusions may be drawn from this study:

1. Oxidized recovered fibers obtained from dissolved air flotation rejects can be used effectively to improve paper physical properties. Tensile index and folding endurance increased by 40.2% and 433.3%, respectively, when the oxidized time was 60 min.

2. The dosage of oxidized recovered fibers plays the most important role in papermaking; tensile index, burst index, and folding endurance, respectively, increased by 71.7 %, 38.5%, and 600% when the dose was 3%. Papermaking worked well when the pH was 5.

3. It is thus clear that oxidized recovered fibers are also effective with recycled paper. Tensile index and burst index were increased by 93.1% and 41.4%, respectively, when the oxidized time was 60 min.

4. The tensile index, burst index, and folding endurance of handsheets with mixture of TOF and CF increased by 2.8%, 4.6%, and 46.8%, respectively, compared with handsheets with only TOF.

5. An SEM micrograph showed that fibers were integrated more closely in the paper sheet, benefiting from the oxidized recovered fibers.

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REFERENCES CITED

Ben, Y. X., Dorris, G. M., and Page, N. (2004). "Characterization of dissolved air flotation rejects," *Pulp Pap. Can.* 105(11), 28-33.

Ben, Y. X., Dorris, G. M., and Page, N. (2006). "Application of column flotation in paper recycling," *Prog. Pap. Recycl*. 15(2), 25-35.

Chaiarrekij, S., Dhingra, H., and Ramarao, B. V. (2000). "Deinking of recycled pulps using column flotation: energy and environmental benefits," *Resour. Conserv. Recy.* 28(3-4), 219-226.

Chen, Q., Song, X. L., Jin X. J., and Qian H. (2012). "Effects of adding recycled fiber from deinked pulp sludge into kraft pulp," *J. Northeast Forestry University* 40(6), 102-104.

China Technical Association of Paper Industry (2009). "2008 Annual report of China's paper industry," *Zhejiang Pulp Paper* 33(2), 1-6.

China Technical Association of Paper Industry (2011). "China paper industry 2010 annual brief," *Paper and Paper Making* 30(7), 71-74.

Hubbe, M. A., Venditti, R. A., Barbour, R. L., and Zhang, M. (2003). "Changes to unbleached kraft fibers due to drying and recycling," *Prog. Pap. Recyc.* 12(3), 11-20.

Hubbe, M. A., Venditti, R. A., and Rojas, O. J. (2007). "What happens to cellulosic fibers during paper making and recycling: A review," *BioResources* 2(4), 739-788.

Ioelovich, M., and Figovsky, O. (2010). "Structure and properties of nanoparticles used in paper compositions," *Mechanics of Composite Materials* 46(4), 435-442.

Katz, S., Beatson, R. P., and Scallan A.M. (1984). "The determination of strong and weak acid groups ID sulfite pulps," *Svensk Papperstidn.* 87(6), R48-R53.

Law, K. N., Daneault, C., and Song, X. L. (2006). "Effect of dichloromethane extraction on properties of chemical fibers," *Cell. Chem. Technol.* 40(6), 439-443.

Song, X. L., and Law, K. N. (2010). "Oxidation of kraft pulp and its influence on the recycling characteristics of fibres," *Cell. Chem. Technol.* 44(7-8), 265-270.

Wang, Y. H., Song, X. L., and Qian, H. (2012). "Carboxymethylation fiber of dissolved air flotation rejects and its influences on paper properties," *Adv. Mat. Res.* 651, 67-72, International Conference on Engineering Materials, ICEM 2012.

Weise, U. (1998). "Hornification-mechanisms and terminology," *Pap. Puu-Pap. Tim.* 80(2), 110-115.

Zhang, M., Hubbe, M. A., Venditti, R. A., and Heitmann, J. A. (2004). "Refining to overcome effects of drying unbleached kraft fibers in the presence or absence of sugar," *Prog. Pap. Recycl.* 13(2), 5-12.

Zhu, J. C., Tangsun. D. R., and Song, X.L. (2011). "Influences of adding nano-materials on paper properties," *Paper and Paper Making* 30 (5), 33-36.

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APPENDIX

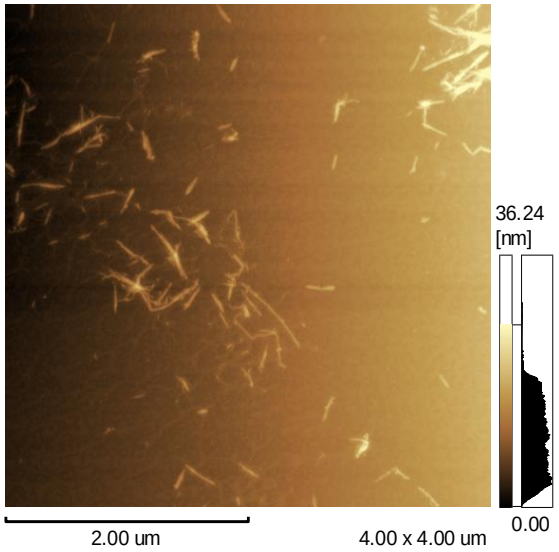


Fig. 4. AFM images of oxidized recovered fibers (8.00×8.00μm)

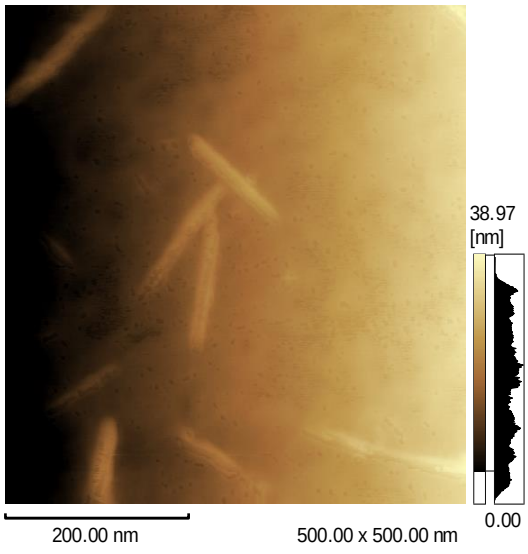
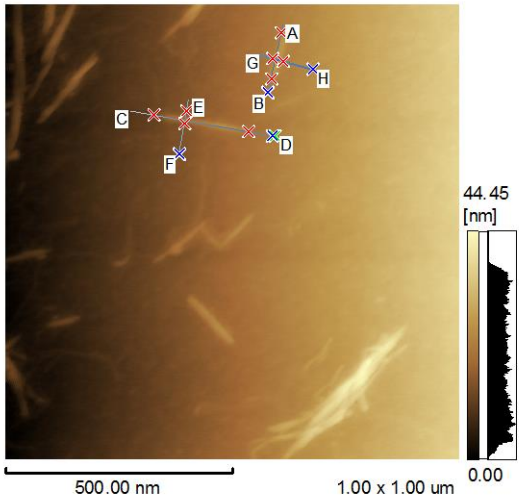
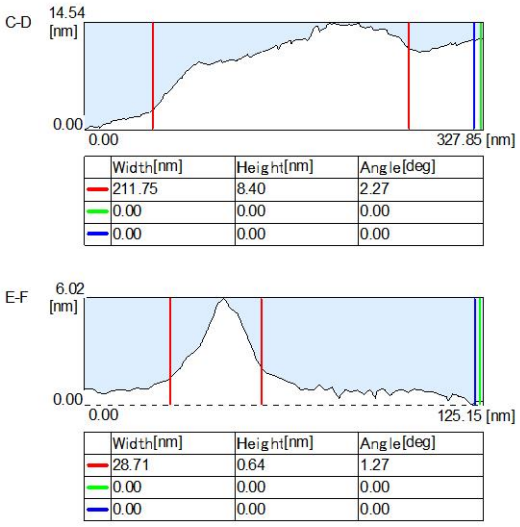
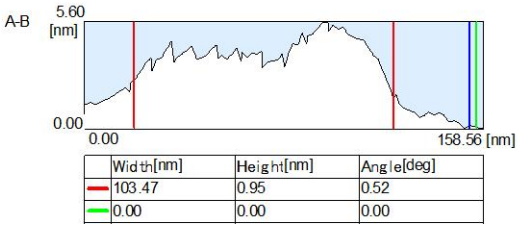


Fig. 5. AFM images of oxidized recovered fibers (500×500nm)







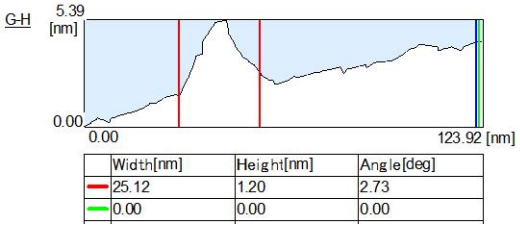


Fig. 6. AFM images of oxidized recovered fibers (1.00×1.00μm)