H_2O_2 Oxidation of Corncob Holocellulose as a Dry-strength Additive for Paper

Tiantian Yang, Weitao He, Sijie Wang, and Xianliang Song*

Corncob, an underutilized agricultural byproduct, was used as the raw material to make a dry-strength additive for paper. Corncob was ground into 80, 100, 150, and 200 mesh powder. The powder was treated with sodium chlorite to remove lignin, and the resulting holocellulose was modified with hydrogen peroxide. The influences of oxidation time, concentration of hydrogen peroxide, dosage of paper strength agent, and the dosage of aluminum sulfate on the paper properties were studied. The results indicate that the oxidized corncobs holocellulose can improve the tensile index, burst index, and folding endurance of paper. Compared with control paper, when the concentration of hydrogen peroxide was 0.9%, the tensile index, burst index, and folding endurance were increased by 24.2%, 14.1%, and 463.8%, respectively. The particle size of raw material, dosage of strengthening agent or aluminum sulfate greatly influences paper properties. Scanning electron microscopy (SEM) analysis showed that the combination between the fibers was improved after adding the strengthening agent, thus improving the strength of the paper. The results can provide a new method for value-added use of corncob.

Keywords: Corncob; Holocellulose; Oxidation; Fiber

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INTRODUCTION

With the improvement of people's living standards, paper consumption has increased. But because of shortage of forest resources, especially long fiber pulp wood, paper companies are using a lot of short fiber pulps such as hardwood pulp, straw pulp, and waste paper. Both the fiber length and fiber bonding strength affect paper properties (Page 1969; Clark 1978; Howard and Jowsey 1989). The bonding strength between fibers can be improved by using dry-strength additives. Due to fiber hornification, the properties of recycled paper tend to be degraded in comparison to the original paper. The properties of recycled paper also can be improved by using dry-strength additives, which can improve inter-fiber bonds of recycled fibers (Hubbe *et al*. 2003, 2007; Hubbe 2006). Paper strengthening agents used currently include starch and its derivatives, polyacrylamide, chitosan, emulsion polymers, and hemicellulose (Ashori *et al*. 2013; Hamzeh *et al*. 2013; Khorasani *et al*. 2013). But some kind of chemical modification is needed to obtain an optimal dry-strength agent (Roberts *et al.* 1987; Denis *et al.* 2003; Pelton 2004; Ren *et al.* 2008, 2009; Fatehi *et al*. 2009; Wang *et al*. 2012).

Hydrogen peroxide oxidation is a method for polysaccharide modification. Under weakly acidic (pH = 5) conditions the hydroxyl groups of polysaccharides are oxidized into aldehyde or carboxyl group by hydrogen peroxide, thereby increasing the carboxyl content of polysaccharides (Park *et al.* 2009). Corncob is an underutilized agricultural byproduct, which is known to contain 65% to 76% of holocellulose. At present, most of

the corncobs (about 40 million tons every year in China) are burned or abandoned. In this work, we used corncobs as raw material, removed lignin by using sodium chlorite, and the resulting holocellulose was oxidized with hydrogen peroxide. The influences of oxidation conditions, particle size of raw materials, and papermaking conditions on the paper properties were studied. The results provide a new method for value-added use of corncob.

EXPERIMENTAL

Materials

The corncob was split into about 20 mm × 15 mm × 10 mm pieces, then the pieces were ground into a fine powder. The powder particles under 80, 100, 150, and 200 mesh size were collected. Kraft pulp of triploid *Populus tomentosa* Carr was prepared under laboratory conditions, which were: liquid ratio 1:4.5, active alkali 16%, sulfidity 25%, maximum temperature 165 ºC, and heating time 2 h. The pulp were beaten to 40 ºSR.

Methods

Preparation of holocellulose

Four grams of corncob powder (dry basis) was put into a 250 mL conical flask. Then 130 mL of distilled water, 20 drops (1 mL) glacial acetic acid, and 1.0 g sodium chlorite were added to the flask. A small conical flask (25 mL) was buckled to the mouth of the larger conical flask. The larger conical flask was then put into a water bath at 75 ºC for 1 h, and the flask assembly was often shaken in the course of the reaction process. Another 20 drops glacial acetic acid and 1.0 g of sodium chlorite were added to the larger flask, then the mixture was reacted for 1 h at 75 ºC. The reaction was stopped by putting the larger conical flask in an ice bath. The mixture was filtered by means of filter paper, washed 4 times with ice water, and then the corncob holocellulose was collected.

H_2O_2 oxidized holocellulose

Ten grams of corncob holocellulose (dry basis) and 286 mL of water were put into a 500 mL conical flask. Then the flask was placed into a 40 ºC water bath; 0.05 g of $FeSO_4$ as catalyst was added, then 30% hydrogen peroxide was added into the conical flask to make different hydrogen peroxide concentrations (0.3%, 0.6%, 0.9%, 1.2% w of hydrogen peroxide / w of solution, respectively). These solutions served as the oxidant to oxidize holocellulose. Dilute sodium hydroxide and dilute hydrochloric acid solutions were used to adjust the pH of the reaction liquid to 5. The reaction time was 60 min with shaking of the flask every 5 min. Upon the completion of the 5 min, the mixture was filtered and washed four times with distilled water. The samples were stored in the plastic bags to maintain the moisture equilibrium.

Carboxyl content

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

Papermaking and physical properties of handsheets

Standard 60 g/m^2 handsheets were prepared and determined according to the appropriate China GB standard methods. The papermaking conditions were as follows: 1% H_2O_2 oxidized corncob, 0.25%, 0.5%, or 0.75% $Al_2(SO_4)_3$ base on dry fibre (w/w) and pH

as given. The step is that: 1% H_2O_2 oxidized corncob holocellulose was put into the pulp at stirring, 0.5% $Al_2(SO_4)_3$ base on dry fibre (w/w) was put into the pulp, then pH was adjusted by H_2SO_4 solution, and the handsheet was made after stirring for 10 min.

FTIR analysis

A certain amount of KBr and the oxidized corncob holocellulose were oven-dried, then ground into powder to obtain a sample suitable for FTIR analysis. Using a Spectrum-100D instrument from PerkinElmer (USA), the absorbance between 4000 cm^{-1} and 400 cm^{-1} was studied.

Elemental analysis

Elemental analysis was carried out by using an Aria EL III instrument. The carbon, hydrogen, and nitrogen contents were tested. Oxygen content was obtained from the total elements, excluding carbon, hydrogen, and nitrogen.

SEM analysis

A S-3000N (Hitachi Ltd, Japan) scanning electron microscope was used for observation of oxidized corncob holocellulose, handsheets surfaces, and fracture surfaces. Gold sputtering was used to avoid charging effects.

Atomic force microscopy (AFM)

The oxidized corncob holocellulose specimens were characterized using a Shimadzu SPn9000 Scanning probe microscopy. Images were collected using a phase mode with a constant force. A droplet of the 1% oxidized corncob holocellulose suspension was dried on a mica surface prior to AFM testing.

RESULTS AND DISCUSSION

Carboxyl Content of Oxidized Holocellulose

The effects of oxidation conditions on the carboxyl content are presented in Table 1. As shown, the carboxyl content did not show evident change with the concentration of hydrogen peroxide, but it increased significantly with increasing duration of the reaction.

Table 1. Effects of Oxidation Conditions on the Carboxyl Content

Concentration of hydrogen peroxide (%)	Reaction time (min)	Carboxyl content ($mmolkg^{-1}$)
0	0	68
0.3	30	70
0.3	60	90
0.6	60	92
0.9	60	93

Notes: The standard deviation is <4%

Elemental Analysis

The elemental contents of corncob holocellulose and oxidized corncob holocellulose are shown in Table 2. The carbon content decreased after oxidation, while hydrogen content increased after treatment. The oxygen content increased first then decreased. This indicates that the oxidation changes hydroxyl groups into carbonyl groups.

Table 2. Effects of Oxidation Conditions on the Elemental Content

	N	C	H	O
Corncob holocellulose	0.230	43.26	6.03	50.48
Oxidized Corncob holocellulose (30 min,H_2O_2 concentration 0.3%)	0.074	42.51	6.04	51.38
Oxidized Corncob holocellulose (60 min, H_2O_2 concentration 0.9%)	0.112	43.00	6.25	50.64

Notes: The standard deviation is <4%

FTIR Analysis

Results from Fourier transform infrared (FTIR) spectroscopy of untreated and oxidized corncob holocellulose by hydrogen peroxide are shown in Fig. 1. Hydroxyl O-H stretching of oxidized corncob holocellulose (the 3434 cm^{-1} peak) decreased relative to that of untreated corncob holocellulose (the 3429 cm^{-1} peak). However the peak at 1738 cm^{-1} (the non-conjugated carbonyl group or a carboxyl group C=O stretching vibration) of oxidized corncob holocellulose increased in comparison to that of untreated corncob holocellulose. The ratio of the OH to C=O decreased from 3.54 (original holocellulose) to 2.43 (oxidized holocellulose), indicating that some hydroxyl groups were changed into non-conjugated carbonyls by oxidized with hydrogen peroxide (Song and Hubbe 2014a,b).

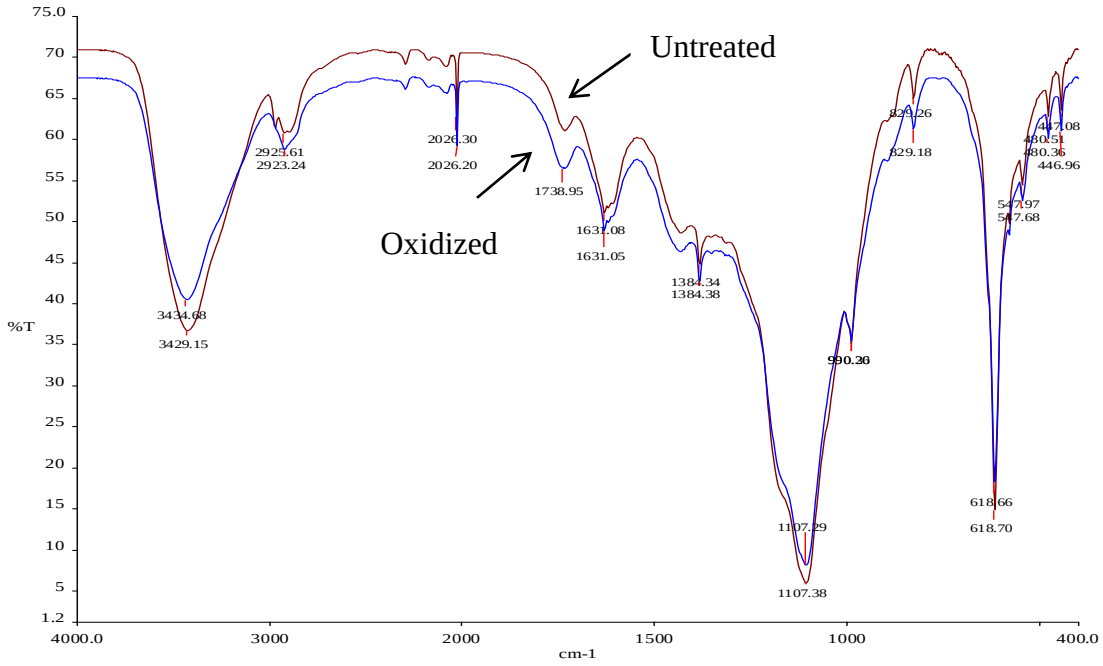

Fig. 1. FTIR spectra of the corncob holocellulose (upper) and oxidized corncob holocellulose (lower)

Effects of Oxidation Conditions on Paper Properties

Effects of oxidation conditions on paper properties are presented in Table 3. As shown, compared with the control sample, the density, tensile index, burst index, tear index, and folding endurance of handsheets with addition of 1% oxidized holocellulose were significantly increased. This can be explained by increases in bonding strength when using oxidized corncob holocellulose. Also, alum alone might increase the strength

properties by better retention of fines, but its effect was not very evident. The oxidized corncob holocellulose had a better effect than the original holocellulose, which was due to the role of nanoparticles of oxidized corncob holocellulose. With the increasing of the concentration of hydrogen peroxide, tensile index, and folding endurance increased initially and then decreased, but density and burst index showed a continual increase. When the hydrogen peroxide concentration reached up to 0.9%, for a 60 minute treatment time, the density increased by 5.2%,the tensile index increased by 24.1%, the burst index increased by 14.1% and the folding endurance increased by 463.8% compared with the control paper (without any chemical additives). The tear index decreased with the increasing of the concentration of hydrogen peroxide; however, tear index increased significantly compare with the control handsheet. This deserves more attention.

Table 3. Effects of the Holocellulose Oxidation Conditions on Paper Properties

H_2O_2 concentration (%)	Reaction time (min)	Density (g/cm^{-3})	Tensile index ($N \cdot m/g^{-1}$)	Tear index ($m \cdot Nm^2/g^{-1}$)	burst index ($KPa \cdot m^2/g^{-1}$)	Folding endurance (double folds)
Control	0	0.405	60.44	7.63	4.03	47
Control*	0	0.406	61.42	7.57	4.06	50
Control**	0	0.407	62.37	7.46	4.08	52
0.3	30	0.410	68.52	9.74	4.43	60
0.6	60	0.416	69.86	8.65	4.47	208
0.9	60	0.426	75.07	8.45	4.60	265
1.2	60	0.429	67.90	7.95	5.34	159

Note: The control sample was prepared with no chemical additives; the other samples were prepared with 1% oxidized corncob holocellulose, 0.5% $Al_2(SO_4)_3 \cdot 18H_2O$ on a dry fiber basis. After alum addition the pH was adjusted to 5. Control* is the sample only with 0.5% $Al_2(SO_4)_3 \cdot 18H_2O$ on a dry fiber basis. After alum addition the pH was adjusted to 5. Control** is the sample with 1% corncob holocellulose, 0.5% $Al_2(SO_4)_3 \cdot 18H_2O$ on a dry fiber basis. After alum addition the pH was adjusted to 5.The standard deviation is <4%

Effect of Corncob Particle Size on Paper Properties

The influence of particle size of corncob powder is shown in Table 4.

Table 4. Effects of Corncob Particle Size on Paper Properties

Raw material particle size (mesh)	Density (g/cm^{-3})	Tensile index ($N \cdot m/g^{-1}$)	Tear index ($m \cdot Nm^2/g^{-1}$)	Burst index ($KPa \cdot m^2/g^{-1}$)	Folding endurance (double folds)
0	0.405	60.44	7.63	4.03	47
80	0.429	67.90	7.95	5.34	159
100	0.430	75.16	8.78	6.40	286
150	0.432	77.40	9.04	7.14	298
200	0.435	77.47	9.02	6.91	333

Note: The oxidized samples were prepared at 1.2% H_2O_2 concentrations, 40 ºC, 60 min. The control sample was prepared with no chemical additives; the other samples were prepared with 1% oxidized corncob holocellulose, 0.5% $Al_2(SO_4)_3 \cdot 18H_2O$ on a dry fiber basis. After alum addition the pH was adjusted to 5. The standard deviation is < 5%

The density, tensile index, burst index, and folding endurance all increased with decreasing of particle size. However, when the particle size was smaller than 150 mesh, the tensile index, burst index, and folding endurance of handsheets did not show a clear trend. This is probably because the smaller of particles, the more particles become nanoscale in the subsequent process of oxidation. The increasing of paper properties can be attributed to a nanomaterial effect, which increased the bonding strength among fibers.

Effects of Dosage of Oxidized Holocellulose on Paper Properties

The influences of dosage of oxidized holocellulose on paper properties are shown in Table 5. The density, tensile index, burst index, and folding endurance exhibited gradual increases with increasing dosage of oxidized holocellulose. The tear index decreased with the increasing of the concentration of hydrogen peroxide; however, tear index increased significantly in comparison with the control handsheet. The results can be explained in terms of an increase in inter-fiber bonding strength with increasing of dosage of oxidized holocellulose. The density, tensile index, burst index, and folding increased by 3.7%, 19.79%, 14.64%, and 491.5%, respectively compared with control when the dosage of oxidized holocellulose was 1.5%.

Table 5. Effects of Strengthening Agent Dosage on Paper Properties

Dosage of oxidized holocellulose (%)	Density (g/cm^{-3})	Tensile index ($N \cdot m/g^{-1}$)	Tear index ($m \cdot Nm^2/g^{-1}$)	Burst index ($KPa \cdot m^2/g^{-1}$)	Folding endurance (double folds)
Control	0.405	60.44	7.63	4.03	47
0.5	0.410	68.26	9.39	4.35	71
1.0	0.416	69.86	8.65	4.47	208
1.5	0.420	72.40	8.81	4.62	231

Note: The control sample was prepared with no chemical additives; the other samples were prepared with oxidized corncob holocellulose (H_2O_2 concentration is 0.6%, reaction time is 60 min), 0.5% $Al_2(SO_4)_3 \cdot 18H_2O$ on a dry fiber basis. After alum addition the pH was adjusted to 5. The standard deviation is < 5%

Effects of $Al_2(SO_4)_3$ Dosage on Paper Properties

The influence of $Al_2(SO_4)_3$ dosage on paper properties is shown in Table 6. The burst index and folding endurance were gradually increased as the dosage of $Al_2(SO_4)_3$ was increased; tensile index increased first and then decreased. A possible reason was that both the pulp fiber surface and the oxidized holocellulose were negative in charge, and therefore they are difficult to be combined due to the repulsive electrostatic forces.

Table 6. Effects of $Al_2(SO_4)_3$ Dosage on Paper Properties

Aluminum sulfate (%)	Density (g/cm^{-3})	Tensile index ($N \cdot m/g^{-1}$)	Tear index ($m \cdot Nm^2/g^{-1}$)	Burst index ($KPa \cdot m^2/g^{-1}$)	Folding endurance (double folds)
0.25	0.410	56.41	8.86	4.34	179
0.50	0.416	69.86	8.65	4.47	208
0.75	0.413	63.58	9.75	4.55	229

Note: The control sample was prepared with no chemical additives; the other samples were prepared with 1% oxidized corncob holocellulose (H_2O_2 concentration was 0.6%, Reaction time was 60 min) on a dry fiber basis. After alum addition the pH was adjusted to 5. The standard deviation was <4%

Al^{3+} has a highly cationic charge, which ties oxidized holocellulose onto fiber surfaces, and this will increase the bonding strength among fibers. But an overdose of aluminum sulfate will lead to decreasing of handsheet properties due to too much cationic charge in the pulp suspension.

Electron Microscopy Images of Corncob Holocellulose

Images of corncob holocellulose and oxidized corncob holocellulose are shown in Figs. 2a and 2b, respectively. As shown, both of corncob holocellulose and oxidized corncob holocellulose consisted of tiny particle aggregates. The particle surface of oxidized corncob holocellulose became wrinkled as a result of surface corrosion in the course of the oxidization process.

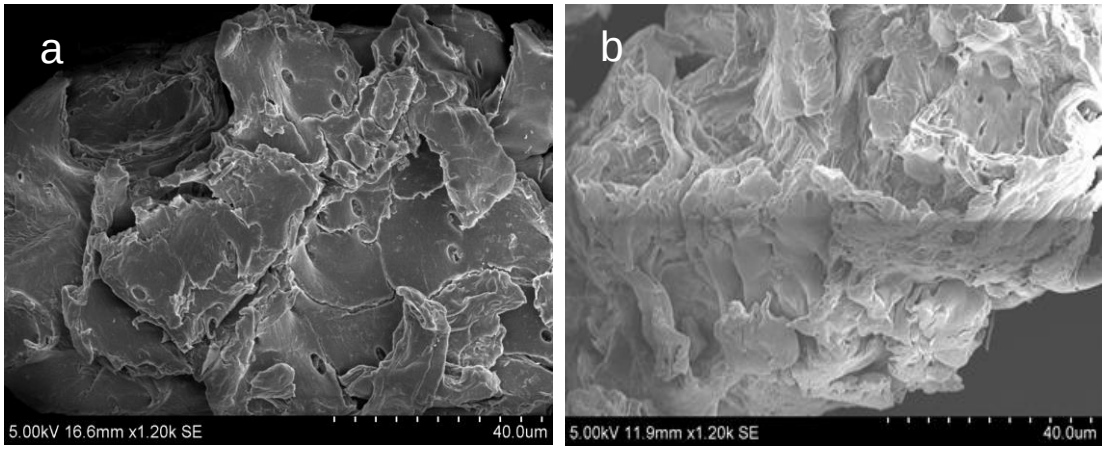

Fig. 2. SEM image of corncob holocellulose and oxidized corncob holocellulose
(a) Corncob holocellulose, (b) H_2O_2 oxidized corncob holocellulose

Electron Microscopy Analysis

SEM fracture images of handsheets without and with H_2O_2 oxidized corncob holocellulose are shown in Figs. 3a and 3b. As shown, the fibers of handsheets with H_2O_2 oxidized corncob holocellulose were different from the control after the handsheets were broken by tensile force.

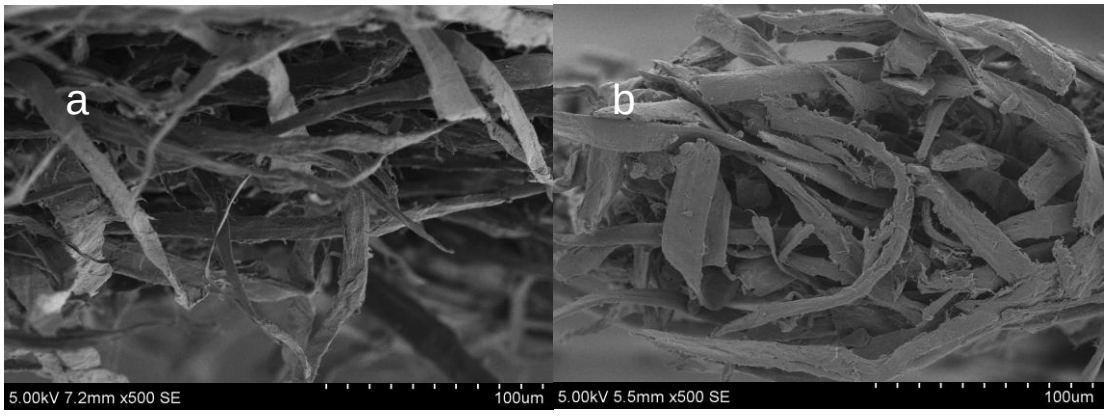

Fig. 3. SEM fracture images of handsheet sample
(a) Control, (b) H2O2 oxidized corncob holocellulose

Most of the edge fibers were intact in the broken control paper, while some of the edge fibers were fractured in the handsheet with H_2O_2 oxidized corncob holocellulose. This result indicates that H_2O_2 oxidized corncob holocellulose can increase inter-fibers bonding in the paper, which causes some fibers to fracture instead of being pulled out from inter-fibers bonding while the handsheet was being broken.

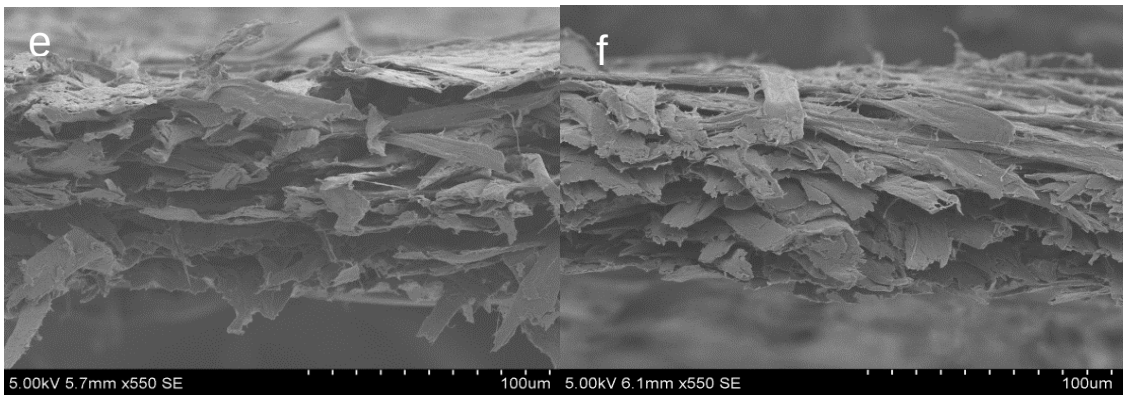

Fig. 4. SEM section and surface images of handsheet sample
(a) Control, (b) H_2O_2 oxidized corncob holocellulose

Cross-sectional images of handsheets sample are shown in Figs. 4a and 4b. As shown, the cross-section of original papers was thicker than that of paper with H_2O_2 oxidized corncob holocellulose. This indicates that the bonding of the fibers in the original paper was loose. This phenomenon can also be explained by the increase of handsheets density, which changed from 0.405 g/cm^{-3} (control paper) to 0.426 g/cm^{-3} (H_2O_2 oxidized corncob holocellulose), see Table 3.

Atomic Force Microscopy (AFM)

The particle sizes of oxidized corncob holocellulose are shown in Fig. 5. As shown, the sizes of most particles were less than 100 nm. Thus the improvement of the paper properties may be described as being due to the role of nanomaterials.

CONCLUSIONS

The following main conclusions may be drawn from this study:

1. The oxidation of corncob holocellulose and its subsequent use as a papermaking additive can improve tensile index, burst index, and folding endurance of handsheets. Compared with control paper, when the concentration of hydrogen peroxide was 0.9%, the tensile index, burst index, and folding endurance were increased by 24.2%, 14.1%, and 463.8%, respectively. This effect was due to increasing of carboxylic content, oxygen content, and nanosize of oxidized corncob holocellulose after the oxidation.

2. The particle size of raw material, as well as the dosage of strengthening agent or aluminum sulfate have great influence on paper properties.

3. Scanning electron microscopy (SEM) analysis showed that the combination between the fibers was improved after adding the oxidized holocellulose, thus improving the strength of the paper.

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APPENDIX

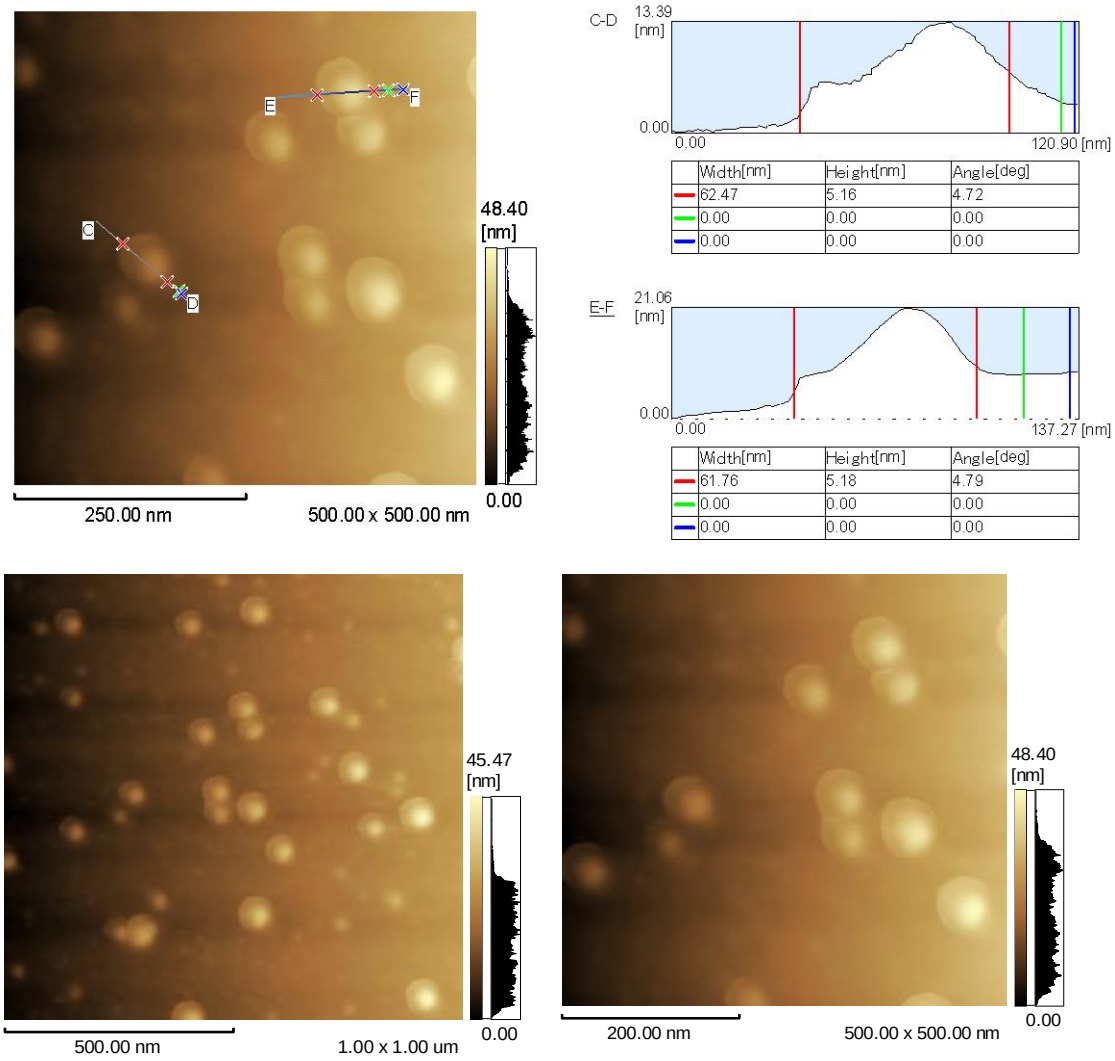

Fig. 5. Atomic force microscopy of oxidized corncob holocellulose