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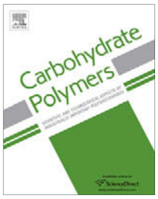

Characteristics of antimicrobial fibers prepared with wood periodate oxycellulose

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ABSTRACT

A kind of antimicrobial fibers, a composite of Chitosan-Dialdehyde Cellulose (C-DAC) fibers, was prepared by using commercially elemental chlorine-free (ECF) bleached kraft softwood cellulose fibers oxidized by periodate and then further grafted by chitosan with different molecular weights. The characteristics of the C-DAC fibers and physical properties as well as antimicrobial activities of the handsheet made of C-DAC fibers were measured. The results show that the dry and rewet tensile indices, antimicrobial activity against *Staphylococcus aureus* and *Escherichia coli*, can be improved significantly as the molecular weight of grafted chitosan on the dialdehyde cellulose fibers decreases.

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1. Introduction

Cellulose is the most abundant and renewable resource in nature. It is widely used in pulp and paper, textile, chemicals, food, medicine, and so on. Its reactivity, versatility, biodegradability, biocompatibility, and low cost meet the requirements for sustainable development of human society.

Chitosan, a partially or completely *N*-deacetylated chitin, mainly consisting of β-(1,4)-2-amino-2-deoxy-D-glucose, is the second most abundant natural biopolymer after cellulose (Vartiainen et al., 2004). Chitosan is also an edible and biodegradable material that has antimicrobial activity against bacteria, yeast, and molds (Cuero, Osuji, & Washington, 1991; Gao, Liu, Liu, Song, & Fan, 2007; Yalpani, Johnson, & Robinson, 1992). Several mechanisms were mentioned for antimicrobial ability of chitosan (El-Tahlawy, El-Bendary, Elhendawy, & Hudson, 2005). They include: (1) the chitosan on the surface of the cell can form a polymer membrane which prevents nutrients from entering the cell (Helander, Nurmiaho-Lassila, Ahvenainen, Rhoades, & Roller, 2001; Zheng, Zhu, & Sun, 2000); (2) the chitosan with lower-molecular weight can come into the cell, bind to the DNA and inhibit RNA and protein synthesis (Liu, Guan, Yang, Li, & Yao, 2001); (3) chitosan could adsorb the electronegative substance in the cell and flocculate them, and disturb the physiological activities of the microorganism leading to death of the cells (Zheng & Zhu, 2003).

Recently, more studies on the application of chitosan were reported (Chen, Yeh, & Chiag, 1996; Helander et al., 2001; Kulpinski, Nishimura, & Tokura, 1997; Zhang, Chen, Ji, Huang, & Chen, 2003). Liu, Nishi, Tokura, and Sakairi (2001) studied the physical properties of a cotton fiber composite with a chitosan coating prepared by the oxidation of a cotton thread with potassium periodate and subsequent treatment with a solution of chitosan in aqueous acetic acid. Wu et al. (2004) prepared the polysaccharides-based membranes of chitosan and cellulose blends using trifluoroacetic acid as co-solvent. They found that the mechanical and dynamic mechanical thermal properties of the cellulose/chitosan blends were almost dominated by cellulose, which suggests that cellulose/chitosan blends are not well miscible. Hosokawa, Nishiyama, Yoshihara, Kubo, and Terabe (1991) studied the reaction between cellulose and chitosan on biodegradable composite film formation, and demonstrated that an increase in the carbonyl groups of cellulose enhances cross-linkings in the composite film formation, while an increase in carboxyl groups does not enhance cross-linkings. El-Tahlawy et al. (2005) used two different cross-linking agents, butanetetracarboxylic acid (BTCA) and Arcofix NEC (low formaldehyde content), to treat cotton fabrics in the presence of chitosan and the treated cotton fabrics showed broad-spectrum antimicrobial activity against Gram-positive and Gram-negative bacteria and fungi. In the work of Montazer and Afjeh (2007), chitosan and *N*-(2-hydroxy) propyl-3-trimethyl ammonium chitosan chloride (HTCC) with different cross-linking agents including CA, BTCA, and glutaraldehyde (GA) were simultaneously applied on the cotton fabric. However, most literature work on the subject required a chemical cross-linking agent or co-solvent when preparing an antimicrobial composite. Furthermore, wood cellulose fibers

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used in pulp and paper industry as a component in the composite have not been well studied yet.

The periodate oxidation of cellulose is characterized by a specific cleavage of the C_2–C_3 bond of the glucose residue. It can produce dialdehyde cellulose (DAC) in which the 1,2-glycol groups of the glucose residues are converted into two aldehyde groups (El Meligy, El Rafie, & Abu-Zied, 2005; Kim, Kuga, Wada, Okano, & Kondo, 2000). The DAC can be utilized as a precursor for many complex compounds (El Meligy & Mobarak, 2005; Kim & Kuga, 2000; Princi et al., 2006). For example, the aldehyde groups of cellulose can be further modified by a Schiff base reaction with amino groups of chitosan, so that chitosan can be grafted onto the oxycellulose fibers. In this grafting reaction no synthetic cross-linking agents prepared using high-molecular weight polymers needs to be added. Furthermore, it may not involve environmental unfriendly chemical reactions. The modified periodate oxycellulose fibers treated with chitosan have antimicrobial capability due to the characteristic of the amino groups of chitosan.

This study demonstrates that an antimicrobial fiber composite of chitosan and periodate-oxidized wood cellulose fiber from the pulp and paper industry can be produced without any requirement of cross-linking agents or co-solvents. This product may be used to produce various biomedical products and antimicrobial package materials.

2. Experimental

2.1. Materials

Commercially elemental chlorine-free (ECF) bleached kraft softwood pulp sheets imported from Chile were used. The characteristics of the pulp are shown in Table 1. The pulp sheets were torn by hand into small pieces roughly 25 mm^2 in size and soaked in tap water for 4 h. Then the wet pulp was dispersed thoroughly in a disintegrator at about 1.2% consistency, and filtered and washed three times with distilled water in a Büchner funnel with a diameter of 200 mm. The prepared fibers with a moisture content of about 75% were stored at temperature of 4–5 °C.

Chitosan with an *N*-deacetylation degree of 86.2% and molecular weight of 6.79×10^6 Da was purchased from Haidebei Marine Bioengineering Co., Ltd. (Jinan, China). *Escherichia coli* (*E. coli*), *Staphylococcus aureus* (*S. aureus*), nutrient agar and peptone were supplied by the School of Bioengineering, Tianjin University of Science and Technology. Distilled water was used throughout the study. All other chemicals used were of analytical grade.

The preparation of phosphate-buffered saline (PBS) solution of pH 7.2: NaCl 8.01 g, Na_2HPO_4 0.61 g, KH_2PO_4 0.19 g, and KCl 0.20 g, were dissolved in 1 L distilled water. Cupriethylenediamine (CED) solution was prepared by following literature method (GB/T1548-2004) (Department of Comprehensive Business, China National Light Industry Council, 2006).

The methanol solution with 0.03 mol/L of sodium hydroxide was prepared by adding 1.200 g of sodium hydroxide into 1 L of methanol. The methanol solution with 20 g/L of hydroxylamine hydrochloride was obtained by adding 20.0 g of hydroxylamine hydrochloride into 1 L of methanol.

Table 1
Characteristics of the commercial bleached kraft softwood pulp

Determined item	Result
Initial beating degree	13.8 °SR
Length weighted fiber length	2.32 mm
ISO brightness	88.6%
Pentosan	⩾5.5%
Ash	⩽0.3%
Resin	⩽0.9%
Tensile index (at 45° SR)	85.08 N m/g

2.2. Apparatus

The standard pulp disintegrator and tensile strength tester (Lorentzen & Wettre, Sweden) were used for dispersing fibers thoroughly in water and for measurement of tensile strength of test sheets. The laboratory handsheet maker (Frank Co., Germany) was used to make paper sheets from fibers. The Fourier-transform infrared spectroscopy (FTIR) (model WQF-510, Beijing Rayleigh Analytical Instrument Co., China), was used to obtain spectra between 375 and 4000 cm^{-1} with 4 cm^{-1} resolution region at ambient temperature. Both the JSPM-5200 atomic force microscope (AFM) and the JSPM-56380LV scanning electron microscope (SEM) (Japan Electron Optics Laboratory Co., Ltd.) were used to analyze the surface structure and morphology of test sheets. The AFM operation was performed at ambient temperature in the tapping mode with a silicon nitride tip and a resolution of 512 pixels × 512 pixels.

The Kjeltec 2300-auto analyzer (Foss Tecator, Sweden) was used to estimate the nitrogen content of chitosan. The seating automatic electrothermal pressure steam sterilizer (Model ZDX-35B, Shanghai Shen An Medical Instrument Manufactory, China) was used to sterilize the glass vessels such as culture dishes, Erlenmeyer flasks and so on. A rocking incubator was purchased from Shanghai WitCity Analyzing Instrument Manufactory Co., Ltd. The electrically heated thermostatic incubator (Model 78-1) was bought from Huangshi Medical Instrument Manufactory (Hubei, China). The Ubbelohde viscometer (Diameter of 0.45 mm) was obtained from Shanghai Asia-Pacific Technic Glass Company (China). The brightness of test sheets was measured using an Elrepho brightness analyzer (Lorentzen & Wetter, Sweden).

2.3. Methods

The DAC fibers were obtained by a periodate oxidation reaction of cellulose fibers and then further grafted by chitosan. The related oxidation and graft reactions in the preparation process of the composite of DAC fibers and chitosan have been reported in literatures (Liu, Nishi, et al., 2001; Vicini & Princi, 2004). Finally, after being treated with sodium hydrosulfite solution, the composite of DAC fibers and chitosan with a relatively stable structure, was obtained.

2.3.1. Periodate oxidation of the cellulose fibers

A 1-L filter flask was used as a reaction kettle. The kettle was put in a water bath after adding 30 g of fibers and 857 mL of 0.08 mol/L sodium periodate solution. The sodium periodate charge on the wood fiber (oven-dry) was 50%. The solution volume included the moisture of the prepared fibers used in reaction. It is equivalent to a total liquid volume of a 30-g (oven-dry) fiber suspension at 3.5% consistency. The pH of the solution was adjusted to about 3.5 using dilute sulfuric acid. The oxidation reaction conditions were carried out at temperature 45 °C. The kettle was wrapped with several layers of aluminum foil to prevent exposure to light. The kettle was pressurized by bottled nitrogen through the exhaust opening of the filter flask while the reaction was in progress. The nitrogen pressure in the kettle was just slightly higher than atmospheric pressure. These measures were to avoid $NaIO_4$ decomposition and photo-oxidation (Fan, Lewis, & Tapley, 2001) and to prevent fiber oxidation by ambient air during periodate oxidation. The rotating shaft of the stirrer passed through a hole at the center of the rubber plug of the filter flask to provide a constant stirring speed of 310 rpm to keep the pulp suspension well mixed during reaction. The clearance between the inside of the center hole of the rubber plug and the outside of the shaft was used as the exhaust opening of the kettle. At the end of reaction of 120 min, the resultant DAC fibers were washed thoroughly with distilled water, and used for the grafting reaction without being dried.

2.3.2. Determination of aldehyde groups and degrees of polymerization (DP) and crystallinity

The content of aldehyde groups in the DAC fibers was determined by converting the dialdehyde cellulose to a nitrogen-containing derivative (oxime) by a Schiff base reaction with hydroxylamine hydrochloride (Kim & Kuga, 2001; Maekawa & Koshijima, 1991). The related reactions and calculation formula are as follows:

$$-\mathrm{CHO} + \mathrm{NH_2OH \cdot HCl} \rightarrow -\mathrm{CHNOH} + \mathrm{HCl} + \mathrm{H_2O} \tag{1}$$

$$\mathrm{HCl} + \mathrm{NaOH} \rightarrow \mathrm{NaCl} + \mathrm{H_2O} \tag{2}$$

$$H = \frac{30X}{w} \ (\mu\mathrm{mol/g\ of\ oven\text{-}dry\ fibers}) \tag{3}$$

H is the content of aldehyde groups of DAC fibers; *X* is the consumed volume of the methanol solution with 0.03 mol/L of sodium hydroxide, in milliliters; and *w* is the weight of oven-dry treated fibers, in grams.

The degree of polymerization (DP) was estimated by the intrinsic viscosity in the following equation (Shi & He, 2003):

$$\mathrm{DP}^{0.905} = 0.75[\eta] \tag{4}$$

where $[\eta]$ is the intrinsic viscosity.

The degree of crystallinity was determined with FTIR based on the O'KI index described with O'Connor experiential formula (Shi & He, 2003), that is

$$\mathrm{O'KI} = \mathrm{a}_{1429}\ \mathrm{cm}^{-1}/\mathrm{a}_{893}\ \mathrm{cm}^{-1} \tag{5}$$

where *a* is spectral intensity.

2.3.3. Preparation of chitosan solution with different molecular weights

The molecular weight and solution viscosity of chitosan vary with the degradation time of that in the acetic acid solution. According to this concept, four different molecular weight chitosan solutions were made. 10.00 g of chitosan was dissolved in 1 L of 1% (v/v) aqueous acetic acid solution in a 2-L beaker with a stirring speed of 300 rpm. The reaction temperature was 95 °C and the reaction duration times were roughly 15 min, 4, 6, and 8 h. At the end of each preset reaction duration time, the solution was cooled down to ambient temperature and filtered by a Büchner funnel, and put into use at once.

2.3.4. Measurements of chitosan solution viscosity and its molecular weight

The viscosity measurement of chitosan solution with different molecular weights was made using an Ubbelohde viscometer that was placed in a glass-made super thermostatic water bath at 30 °C. According to the result obtained, the molecular weight of the chitosan can be estimated using the following Mark-Houwink equation:

$$[\eta] = \mathrm{KM}^{\alpha} \tag{6}$$

where *K* and α are two empirical parameters related to the structure and solvent of chitosan. Here, *K* is 0.0474 mL/g and α is 0.723, which is reported in the literature (Tan & Du, 2002). The chitosan with four different molecular weights ranged from 0.64×10^6 to 6.79×10^6 Da was obtained.

2.3.5. Grafting chitosan onto the DAC fibers

After adding 1 L of chitosan solution with different molecular weights in a 2-L beaker, and placing the beaker in an 80 °C water bath with stirring speed of 280 rpm, the 20.0 g (oven-dry) of DAC fibers were then dispersed in the chitosan solution, which gave the weight ratio of chitosan to DAC fibers of 1:2. When 30 min were left of the whole 2 h reaction duration time, 25 mL of 0.2 mol/L sodium hydrosulfite solution was added into the beaker to obtain a relatively stable structure of the reaction product. After finishing the reaction, the DAC fibers treated with chitosan solution and sodium hydrosulfite were filtered in a Büchner funnel and washed with distilled water thoroughly. Then the fibers were well dispersed in the disintegrator at 1.2% consistency for 15,000 revolutions. Wash and filter once more to obtain the DAC fibers grafted onto by chitosan with different molecular weights. They were named C-DAC/A, B, C, and D, based on the size of the molecular weight of chitosan.

2.3.6. Kjeldahl nitrogen determination of C-DAC

The Kjeldahl method can measure nitrogen in the trinegative state in certain organic compounds. It is used for determining the content of chitosan with different molecular weights grafted on the DAC fibers in this study. The content of nitrogen was calculated by the formula (Persson, 2001):

$$\mathrm{N\%} = \frac{(T - B) \times N' \times 14.007 \times 10^{-3} \times 100}{w} \tag{7}$$

where *T* is the volume of hydrochloric acid solution (HCl) used in titration for C-DAC fibers, in milliliters; *B* is the volume of HCl solution used in titration for DAC fibers, in milliliters; *N*' is the concentration of standard HCl solution, in mol/L; *w* is the weight of testing sample, in grams.

The chitosan content grafted on the DAC fibers was calculated as follows:

$$A = \frac{\mathrm{N\%}}{14.007} \times 166.74 \tag{8}$$

2.3.7. Testing of the physical properties of handsheets

The handsheets were made of untreated, DAC and C-DAC fibers, respectively. The handsheets preparation and the analysis for the physical properties investigations, such as dry and rewet tensile strengths, elongation rate, TEA, were performed according to the literature methods (Shi & He, 2003).

2.3.8. Cultivation of the microorganism

At first all of Erlenmeyer flasks with/without the LB liquid medium (peptone 1%, yeast extract 0.5%, NaCl 1%, and pH 7.5), culture dishes, PBS solution, graduated cylinders, distilled water, etc., were placed into the sterilizer (0.103 MPa, 121 °C, 20 min) for sterilizing. *E. coli* and *S. aureus* were put separately into an Erlenmeyer flask with 25 mL of the medium. Then they were incubated overnight on a shaking table (37 °C, 160 rpm, 12 h). The cultures obtained were diluted with autoclaved water to obtain *E. coli* and *S. aureus* suspensions with seven different concentrations ranged from 10^{-7} to 10^{-1}.

The handsheets made of C-DAC and DAC fibers were cut into 15 mm × 15 mm pieces, 0.500 g of them were weighed and put into a 250 mL Erlenmeyer flask with 99 mL of PBS solution and 1 mL of diluted *E. coli* and *S. aureus* suspensions, respectively. Then the flasks were placed on a shaking table (37 °C, 120 rpm, 1 h) to evaluate the antimicrobial ability of the handsheets.

The LB solid medium (peptone 1%, yeast extract 0.5%, NaCl 1%, nutrient agar 1.2%, and pH 7.5) was heated until it was totally melted. After the medium was cooled down to about 55 °C, about 15 mL of the medium was poured into each numbered and sterilized culture dishes. One milliliter of the bacterial suspension was taken and carefully dropped into the center of the medium surface. A sterile glass coater was used for keeping the coated surface as uniformly as possible. Finally the culture dishes were put in the incubator at 37 °C for 24 h and the surviving cells were counted. The average values of the duplicates were converted to colony forming units per milliliter.

The percentage reduction of bacteria can be calculated by the following equation:

$$R\% = \frac{A - B}{A} \times 100 \tag{9}$$

where A and B are the bacteria amount per milliliter for the control (DAC fibers) and C-DAC fibers test samples, respectively.

3. Results and discussion

3.1. Properties of oxycellulose by periodate oxidation

The aldehyde groups content of the oxycellulose reflects not only the oxidative extent of the cellulose fibers oxidized by periodate but also the extent of chitosan grafted. An appropriate periodate oxidation condition for the cellulose fibers was chosen (Hou, Liu, Liu, & Bai, 2007) and the results produced were shown in Table 2. The aldehyde groups content of the DAC fibers could reach 1.88 mmol/g dry fibers after sodium periodate oxidation. However, the degree of polymerization and the brightness of the DAC fibers decreased as oxidation proceeded.

3.2. Grafting reaction of chitosan with DAC fibers

When the Schiff base reaction between the aldehyde groups of DAC fibers and the amino groups of chitosan takes place, the chitosan with different molecular weights can be linked on the DAC fibers. The nitrogen and chitosan contents of the chitosan-DAC (C-DAC) fiber composite both increase as chitosan molecular weight decreases (Fig. 1). Both contents reached their respective maximum values at chitosan molecular weight 0.80 × 10^6 Da. This suggests that chitosan with a high-molecular weight was mostly adsorbed on cellulose fiber surface to partially or completely link the fibers. Chitosan with a low-molecular weight, however, could further enter the space between the fibers to increase the probability of contacting and even reacting with the cellulose fibers. The C-DAC fibers with high nitrogen and chitosan contents could be obtained because of a weakly steric hindrance effect during the reaction between DAC fibers and the chitosan with a low molecular weight. Further decreasing the molecular weight below 0.80 × 10^6 Da, the nitrogen and chitosan contents of C-DAC fibers both decreased slightly. This might be due to the decrease in the content of amino groups on the chitosan molecular as the chitosan molecular weight decreased.

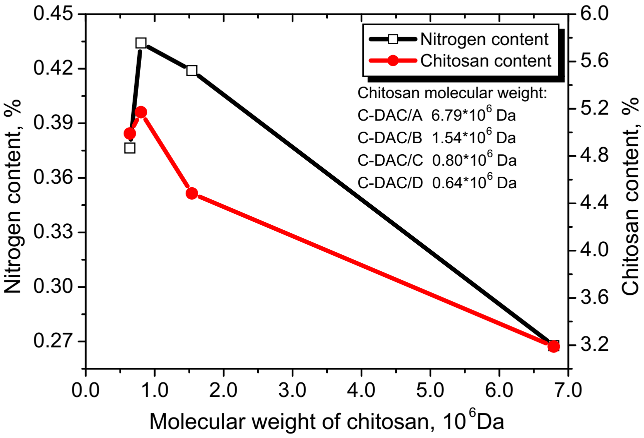


Fig. 1. Nitrogen and chitosan contents on C-DAC fibers.

3.3. Physical properties of C-DAC fibers

3.3.1. Dry and rewet tensile indices of C-DAC handsheets

The dry and rewet tensile indices of the handsheets made of DAC fibers and C-DAC fibers were investigated and the results were shown in Fig. 2. It is clear that the DAC fibers had higher dry tensile index due to the presence of the aldehyde groups and the condensation reaction with the hydroxy groups during handsheet making. The effect of condensation reaction was summarized by Saito and Isogai (2005). For the C-DAC fibers, however, some aldehyde groups had been linked to amino groups of chitosan and were no longer available. As a result, the relative bonding area between fibers was less than that of DAC fibers. This is why both the dry and rewet tensile indices of the handsheets made of C-DAC fibers were, respectively, lower than those of handsheets made of DAC fibers. Fig. 2 also shows that both the dry and rewet tensile indices for the C-DAC fibers increased as the molecular weight of chitosan linked on the DAC fibers decreased, and reached a maximum value at molecular weight 0.80 × 10^6 Da. The maximum dry and rewet tensile indices are 10.7 and 2.7 N · m/g, respectively. This could be attributed to the content of chitosan grafted onto the DAC fibers.

Table 2
Properties of the cellulose fibers before and after periodate oxidation

Before/after oxidation	Aldehyde groups content (mmol/g dry fibers)	Degree of polymerization (DP)	Crystallinity index (O'KI index)	Brightness (%ISO)
Before	0	1142	1.34	88.6
After	1.88	96.5	1.19	85.6

3.3.2. Elongation rate and tensile energy adsorption (TEA) of the handsheets made of C-DAC fibers

The elongation rate and TEA are two of the main parameters for paperboard packing materials. Both parameters of the handsheets made of C-DAC fibers were measured as shown in Fig. 3. The same tendency as the dry and rewet tensile indices could be found in the figure. This demonstrated that the chitosan molecules could be dispersed in the amorphous area of DAC fibers and then adsorbed on the surface of the fibers (Lertsutthiwong, Chandrkrachang, Nazhad, & Stevens, 2002). During handsheets drying, the chitosan would

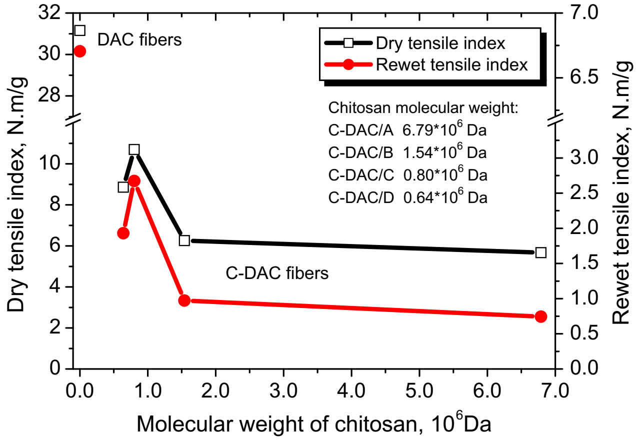


Fig. 2. Dry and rewet tensile indices of handsheets made of DAC and C-DAC fibers.

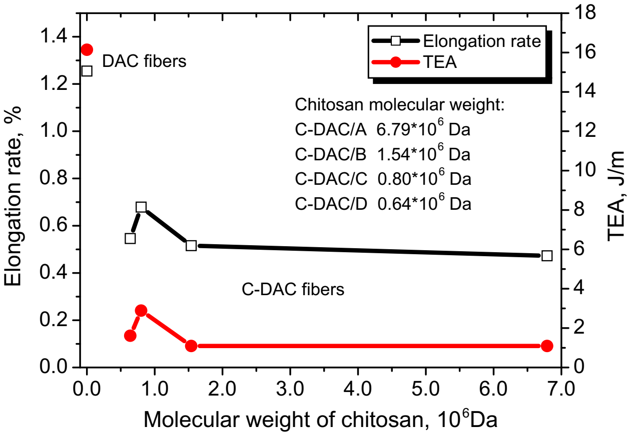


Fig. 3. Elongation rate and TEA of handsheets made of DAC and C-DAC fibers.

act as a coupling agent to bind C-DAC fibers each other and to enhance the bonding strength between the fibers. However, both the elongation rate and TEA of the sheets made of C-DAC fibers were less than the sheet made of DAC fibers due to the steric hindrance effect of chitosan molecules.

3.3.3. Brightness of handsheets made of C-DAC fibers

The brightness of the C-DAC fibers can reflect the relative content of grafted chitosan molecules. The higher the nitrogen content of the C-DAC fibers, the higher the content of grafted chitosan, therefore, the lower the brightness of the test sheet. The minimum brightness was observed in this study at the chitosan molecular weight 0.80×10^6 Da (sample C-DAC/C), corresponding to nitrogen content 0.43%.

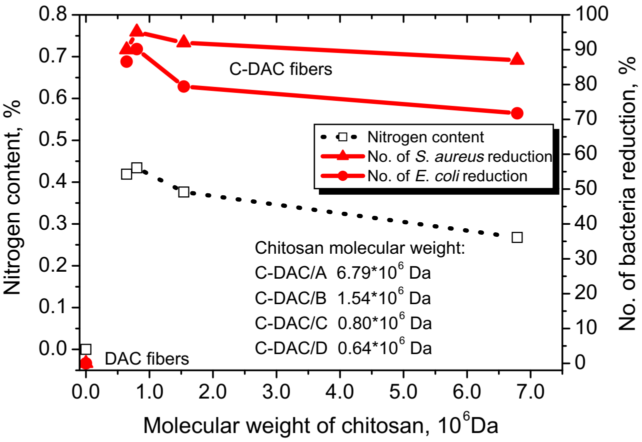


Fig. 4. Inhibition ability of DAC and C-DAC fibers against *E. coli* and *S. aureus*.

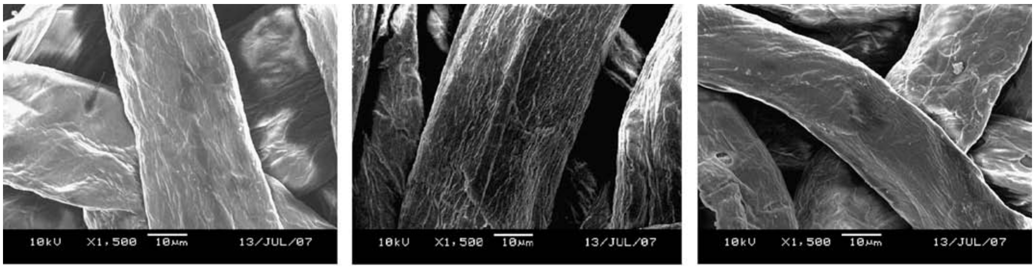
3.4. Antimicrobial ability of C-DAC fibers

Fig. 4 shows the antimicrobial ability of the handsheets prepared with C-DAC fibers. The percentage of the bacteria number reduction increases as the nitrogen or the grafted chitosan content of C-DAC fibers increases. The highest value of the reduction percentage for both *E. coli* and *S. aureus* was resulted from the test sheet made of C-DAC fibers with the highest nitrogen or chitosan content. The reduction percentage for *E. coli* and *S. aureus* was 90.2% and 95.1%, respectively, corresponding to bacteria number on the respective control test sheets of 78×10^7 and 55×10^7 per milliliters. This result indicates that C-DAC fibers have a highly inhibitory effect on the bacteria of *E. coli* and *S. aureus*. In addition, C-DAC fibers proved more effective to inhibit the growth of *S. aureus* than the growth of *E. coli* due to the difference in their bacterium cell structures. The reduction numbers of 90.2% and 95.1% in *E. coli* and *S. aureus* are high enough that can significantly reduce health risk or improve food safety if the paper is used for packaging.

The validity of an inhibitory effect on bacteria of *E. coli* and *S. aureus* for a composite of C-DAC fibers shows that the modification method of cellulose fibers in this study is feasible when preparing antimicrobial fibers. Moreover, the problem that cellulose/chitosan blends have not been well miscible when using a co-solvent or a cross-linking agent may be resolved.

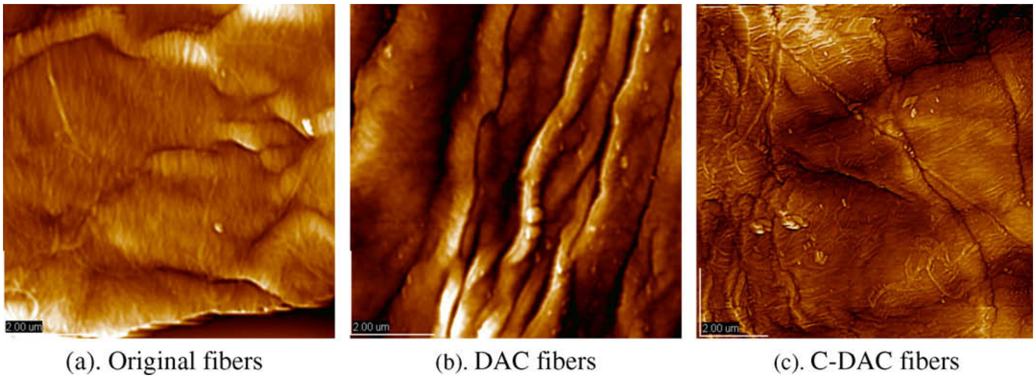
3.5. SEM and AFM analyses of the test sheets

To further explore various effects of periodate and chitosan treatments in the cellulose fibers, a series of the test sheets made of the original, DAC and C-DAC fibers were subjected to SEM and AFM analysis. The results indicate that the original fibers have a rather smooth appearance (Fig. 5a), while the DAC fibers have some microfibrils stick out from the surfaces (Fig. 5b). After grafting of chitosan, the surface of C-DAC fibers becomes smooth, and the distribution of chitosan looks like a grain (Fig. 5c). The result of the AFM investigation (Fig. 6) is similar to that of the SEM analysis. The AFM topographical images acquired show dramatic changes in fiber morphology. Fig. 6a presents an AFM micrograph of a small piece of control test sheet made of the original fibers. Most of the fiber surfaces are nearly flat and relatively smooth and have few wrinkles. Fig. 6b displays a topographical image of the test sheet prepared by DAC fibers. Orientated, wrinkled, closely interwoven microfibrils can be clearly seen as a result of periodate oxidation, hydration and drying. The increase in surface roughness and the number of closely interwoven microfibrils can expand fiber bonding area. The sheet made of C-DAC fibers (Fig. 6c) is not like the sheet made of DAC fibers because the steric obstacle of the



(a). Original fibers (×1500) (b). DAC fibers (×1500) (c). C-DAC fibers (×1500)

Fig. 5. SEM analysis of the original, DAC and C-DAC fibers.



(a). Original fibers (b). DAC fibers (c). C-DAC fibers

Fig. 6. AFM investigation of the original, DAC and C-DAC fibers.

chitosan linked on the DAC fibers hampers the bonding between the fibers.

4. Conclusions

Antimicrobial fibers, a composite of Chitosan-Dialdehyde Cellulose (C-DAC) fibers, can be produced using oxycellulose fibers (DAC fibers) oxidized by periodate and then grafted by chitosan with different molecular weights. For the given DAC fibers, the chitosan content of C-DAC fibers increases as chitosan molecular weight decreases. The highest chitosan content can be obtained using chitosan with molecular weight 0.80×10^6 Da for a molecular weight range from 0.64×10^6 to 6.79×10^6 Da studied. Meanwhile, the optimum properties of the DAC fibers, such as the dry and rewet tensile indices, elongation rate, TEA, and antimicrobial activity, were also achieved. The highest dry and rewet tensile indices were 10.7 and 2.7 $\mathrm{N \cdot m/g}$, respectively. The C-DAC fibers have a highly inhibitory ability against *E. coli* and *S. aureus*, and the bacteria number reduction percentage for *E. coli* and *S. aureus* could reach 90.2% and 95.1%, respectively. The brightness of the C-DAC fibers, however, may decrease significantly due to grafting reaction. This kind of fibers can be used as an antimicrobial packaging material without requirement of high brightness.

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