Structure and Properties of Cu(II) Complex Bamboo Pulp Fabrics

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ABSTRACT: Cu(II) complex bamboo pulp fabric (CBPF) was prepared by treating bamboo pulp fabric with the copper liquor. Washing fastness and the releases of Cu(II) were measured by the washing test. Antibacterial performance of CBPF against *Escherichia coli* and *Staphylococcus aureus* was evaluated. The morphology of Cu(II) on the fiber surface was characterized with scanning electron microscope. FTIR spectroscopy and X-ray photoelectron spectrometry were used to detect the chemical bonding between Cu(II) and cellulose. X-ray diffraction, thermogravimetry and mechanical test were used to investigate the effect of Cu(II) on the crystallinity, thermal stability, and mechanical property of bamboo fabric. The results showed that Cu(II) ion was bonded to fiber surface, especially via forming metal complex with hydroxyl of cellulose, and the resultant complex CBPF demonstrated excellent antibacterial activity and good thermal stability. In comparison with those of the bamboo pulp fabric in the condition that mechanical properties have no significant change, the crystallinity was decreased from 44.8% to 40.5% after treatment. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 1843–1850, 2010

Key words: biofibers; compounding; crosslinking; microstructure; modification

INTRODUCTION

There is a growing tendency to utilize natural fiber plants. Bamboo is a woody herbaceous plant and consists of many vascular bundles and xylem. Cellulose content in bamboo is about 57–66%, and especially α-cellulose gets around 26–43% that is comparable with that of softwoods and hardwoods.[1] There are 1250 species of bamboos within 75 genera in the world. Among the rest, Asia accounts for 1000 species or so, covering an area of over 180,000 km^2. Bamboo is a kind of rapidly grown and early harvested vegetable with high adaptability, which is not like tree to suffer insect infestation. Bamboo is mainly employed in conventional applications such as furniture, construction, paper industry, in spite of its superior properties like biodegradability, inexpensiveness, and renewability.[1–3]

Bamboo pulp fiber has been successfully made in China, which belongs to green and environment-friendly fiber, for it is a biodegraded polymer and can be yielded without pollution in the processing. Bamboo pulp fiber is made from cellulose of bamboo in the form of dissolving pulp, and then it is turned into something like viscose fiber via spinning. However, it is very different from conventional viscose fiber in the raw material and procedure. Generally, bamboo pulp fiber has lost the antibacterial property lain inherently in bamboo resulting from the treatment with alkali in the processing.[4,5]

It is well known that Ag(I) is frequently used as antibacterial agent. Positively charged silver ions attracted to electronegative bacterial cells are bonded to their membrane or bacterial DNA with sulfhydryl groups, resulting in the prevention of proliferation of bacteria and blockage of biofilms. Microorganisms, resistant to the antimicrobial activity of silver, are exceedingly rare. Besides silver, the other metal ions such as Cu(II), Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Zn(II), Cd(II), Hg(II), and Pd(II) show strong biocidal effects on many pathogenic bacteria too.[6–11] Among them, Cu(II) is distinctive since it not only can be used as an important antibacterial agent for textiles but also plays a key role in collagen crosslinking in biomedical application.[6,12–16] There are two techniques to prepare antibacterial fiber principally. One is to blend antibacterial agent with polymer to cospinning, and the other is to treat the fiber surface with antibacterial agent via physical and chemical absorption. The latter is simpler than the former.

It was reported that a novel cellulose-based fiber, obtained by periodate-induced oxidation of cotton fiber to give dialdehyde cellulose, followed by covalent attachment of $-NH_2$ group of chitosan through coupling reaction. The fiber was used for the immobilization of Cu(II) and copper nanoparticles to

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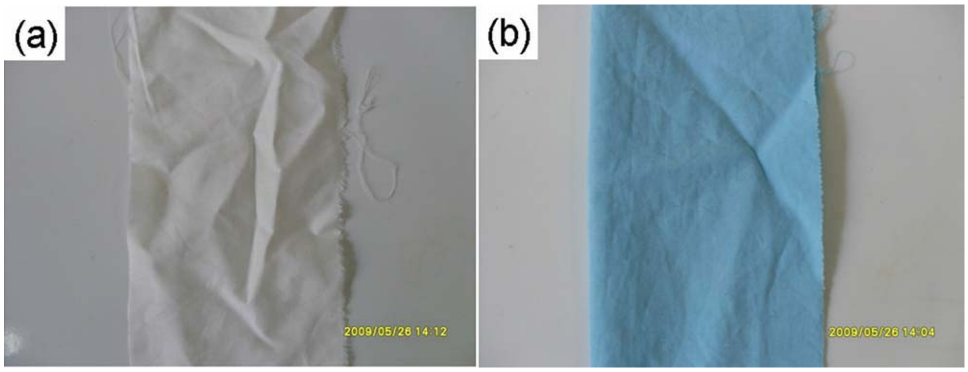

Figure 1 Photographs of (a) bamboo pulp fabric and (b) Cu(II) treated. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

realize fair antibacterial property.[6] Cu(II) complex with conventional viscose fiber was reported to present a good antibacterial property against *Staphylococcus aureus*. It was spectacled that Cu(II) complex cellulose was in the form of coordination structure of CuO_4, which was a planar coordination compound in square configuration.[14]

The significance of this study is to achieve a novel biofiber Cu(II) complex bamboo pulp fiber, which is wholesome and comfortable fitting the tendency of development in fiber. It is taken Cu(II) as antibacterial to endow bamboo pulp fabric with antimicrobial performance. And then, the way of how to anchor Cu(II) ion to bamboo pulp fiber tightly is probed in the condition that mechanical properties of bamboo pulp fabric keep intact during the processing. Here, Cu(II) complex bamboo pulp fabric (CBPF) is prepared via treating the fiber surface with copper liquor in lower concentration that can not dissolve the cellulose fiber. This is a simple way to carry out and the study has not been conducted yet.

Bamboo pulp fiber has widely applied in textile industry to produce dry goods. As an antibacterial fiber, CBPF may be used as not only a textile material but a medical one. It can produce underwear, footgear, decorating fabric, medical fabric, sanitary articles, packing materials, etc. But Cu(II) has its own adverse effects on human body and it would be careful to be utilized. It should be inhibited from using for infant.

EXPERIMENTAL

Materials

Bamboo pulp fabrics chosen were purchased from Tanzhuzhuang Bamboo Fiber in Anji, Zhejiang, China, which was bleached and scoured. Its color was white with a density of 138 g/m^2 and a thickness of 0.29 mm as shown in Figure 1(a). All other chemicals used were purchased from Sinopharm Chemical Reagent, China, as analytical reagents and employed without further purification.

Preparation of CBPF

CBPF, i.e., Cu(II) complex bamboo pulp fiber, was prepared by Cu(II) treated bamboo pulp fabric. The preparation was divided into three parts. First, the bamboo pulp fabric was soaked in 0.25*M* NaOH aqueous solution for 20 min at room temperature to remove the oil and impurities, and then washed with tap water cleanly. Second, $Cu(OH)_2$ precipitation was formed via reacting 1*M* $CuSO_4$ aqueous solution with 2*M* NaOH aqueous solution at equal volume and then filtrated. Copper liquor was obtained by the means that the $Cu(OH)_2$ precipitation was dissolved totally in ammonia water with the ratio of 1 : 3. The cuprammonium ion, i.e., $[Cu(NH)_4]^{2+}$ was formed. Copper liquor was made in a concentration of 0.05*M*, which was dark blue solution with pH 12 or so, using to treat bamboo pulp fabric. Third, the bamboo fabric was immersed in the copper liquor of 0.05*M* at a bath ratio of 1 : 30 and the solution was oscillated gently at room temperature for 20 min and then the fabric was rinsed thoroughly with tap water several times to remove the unfixed ones. After that, the fabric was air-dried for about 20 min at 70°C and cooled down to room temperature. The CBPF was obtained with blue color and a density of 147 g/m^2 and a thickness of 0.31 mm as shown in Figure 1(b).

Washing fastness

Washing fastness was carried out according to Chinese standard FZ/T 73023-2006 (Appendix C),[17] China. The washing liquor was detergent aqueous solutions at concentrations of 2 and 5 g/L, respectively. CBPF and the liquor with a bath ratio of 1 : 30 at 40°C were charged. Washing times were varied from 30 to 60, 90, 120, 150, 180, 210, 240, 270, and

300 min (30 min every cycle). The samples were cleaned with tap water after every cycle. The samples were finally air-dried for about 30 min at 70°C. Some of the samples after washing were used to analyze Cu(II) content quantitatively.

The unwashed CBPF sample was taken as reference one. The weighed sample with 50 mg, was dissolved in 10 mL nitric acid (65 wt %), and then the solution was diluted by deionized water to 10 times. The concentration of Cu(II) in the solution named C_1 (Cu(II) mg/L) was measured at Cu 327 nm using Vista MPX (USA). Upon C_1, the Cu(II) content of the CBPF in percentage concentration (C_2) was calculated as follows:

$$C_2(\%) = C_1/5$$

To investigate dynamic release of Cu(II) from the CBPF, the content of releasing Cu(II) out of CBPF was estimated by the same washing test. The content of releasing Cu(II) out of CBPF(C) is estimated by:

$$C = C_0 - C_2$$

where C_0 was the concentration of Cu(II) for the reference one, Cu(II) mg/g CBPF; C_2 was the content of Cu(II) in CBPF as described above, but here in the unit of Cu(II) mg/g CBPF.

Assessment of antibacterial performance

Antibacterial performance of the CBPF against *Staphylococcus aureus* (*S. aureus*) and *Escherichia coli* (*E. coli*) was determined according to appendix D of FZ/T 73023-2006.[17] The test procedure was that the sample fabric (0.75 g), cut into small pieces in a size around 0.5×0.5 cm^2, was dipped into a flask containing 70 mL of 0.3 m*M* PBS (monopotassium phosphate, pH $\approx$ 7.2) culture solution with a cell concentration of 3×10^5 to 4×10^5 cfu/mL. The flask was then shaken at 150 rpm on a rotary shaker at 24°C for 18 h. From each incubated sample, 1 mL of solution was taken, diluted, and distributed onto an agar plate. All plates were incubated at 37°C for 24 h and the colonies formed were counted. The antibacterial performance of the fabric was expressed in the percentage antibacterial as follows:

$$\text{Percentage antibacterial}(\%) = 100 \times (A - B)/A$$

where A was the amount of bacterial colonies out of the original bamboo pulp fabric and B was the amount out of CBPF.

To make sure that the bamboo pulp fabric had no antibacterial activity, the reference fabric–cotton fabric, was also tested in the same way.

Morphology analysis

Scanning electron microscopy (SEM) was used to observe longitudinal surface morphology. The samples were golden coated. The instrument was a JEOL JSM-5600LV electron microscopy with an accelerating voltage of 15 kV.

X-ray diffraction analysis

X-ray diffraction (XRD) patterns of the treated and untreated bamboo pulp fabrics were obtained with a model D/MAX3C X-ray detector diffraction system at a voltage of 40 kV, a current of 30 mA, and a scan rate of 2°/min. The crystallinity of the bamboo pulp fabrics was calculated by the method of peaks separation and Gaussian peak fit with peakfit v. 4.12.[18] The formula was as follows: $X_c = [I_c/(I_c+I_a)] \times 100\%$. Where X_c was the crystallinity of the fabric, I_c was the sum of all crystal peaks diffraction intensity, and I_a was the diffraction intensity of amorphous peak.

TG analysis

Thermogravimetric analysis was carried out on a Diamond DSC (Perkin-Elmer, USA) under a constant nitrogen flow of 20 mL/min from 40 to 600°C at a heating rate of 10°C/min.

FTIR spectroscopy

Infrared spectra of the bamboo pulp fabric and CBPF were recorded on a Nicolet 5700 FTIRspectrophotometer using KBr disk. The measurements were performed at 20°C and a relative humidity of 65%.

X-ray photoelectron spectrometry

X-ray photoelectron spectrometry (XPS) analyses were carried out on a XSAM 800 electron spectrometer (Kratos, UK). The samples were analyzed using MgK_α radiation (1253.6 eV) operating at a working pressure of 2×10^{-7} Pa in 0.1 eV steps with 100 eV analyzer pass energy. The position of the carbon peak (284.8 eV) for C1s was used to calibrate the XPS scale for all substrates.

Mechanical properties

Tensile strength and elongation at break of the fabrics were realized at YG026B Electronic fabric strength tester (Ningbo Textile Instrument Factory, China) according to ISO 13934-1. Test length was 30 cm and speed was 200 mm/min. The samples were conditioned in a room (20°C, a relative humidity of 65%) for 48 h before measurement.

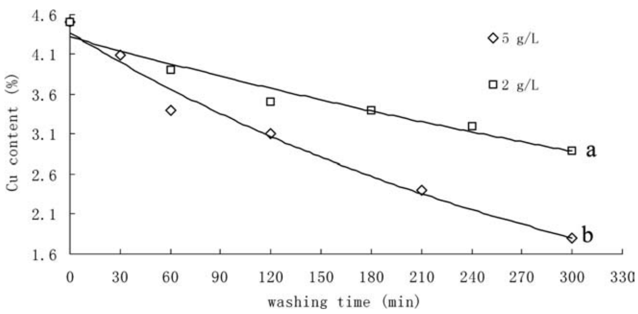

Figure 2 Washing fastness of CBPF: (a) □, 2 g/L and (b) ◇, 5 g/L; washing time (min) and Cu content (%).

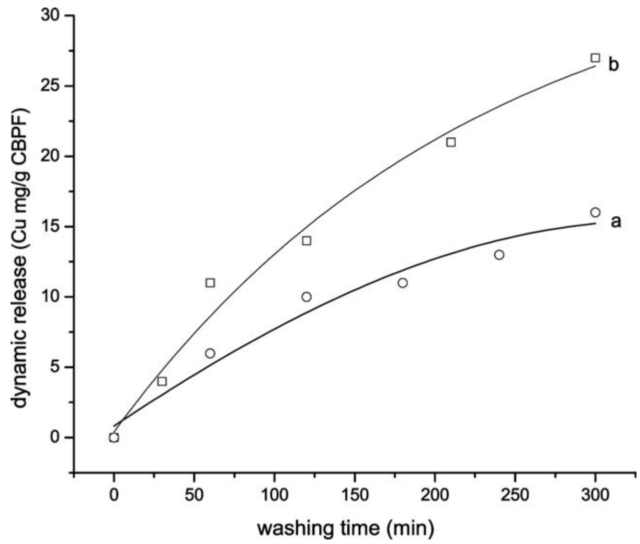

Figure 3 Dynamic release of Cu(II) from CBPF: (a) ○ and (b) □; washing time (min) and Cu(II) releasing Cu(II) mg/g CBPF.

RESULTS AND DISCUSSION

Washing fastness and Cu(II) release study

Figure 2 shows the Cu(II) content changes with washing total times from 0 to 300 min in the detergent concentrations of 2 g/L (a) and 5 g/L (b), respectively. As presented in Figure 2, the Cu(II) content of the CBPF before washing was 4.5% (wt), i.e., $C_0 = 45$ mg/g. This is a high value compared with that of Ag(I) which was below the amount of 0.5% (wt) to the fiber,[7,19] indicating bamboo pulp fabric has a good absorbing activity toward Cu(II). In curve (a), the content of Cu(II) decreased to 2.9% with washing time 300 min in 2 g/L; in curve (b), the content of Cu(II) decreased to 1.8% in 5 g/L. Curves (a) and (b) decline in exponential decay in second order with correlation coefficient being 0.9915 and 0.9893. Obviously, the Cu(II) content decreases more rapidly in the 5 g/L than in the 2 g/L in accordance with common lavation sense.

CBPF displays a laundry resistant property. So it has a good premise to be applied. It may imply that there is a good physical absorption by van der Waals forces and/or there exists chemical binding between Cu(II) and cellulose in CBPF.

Dynamic release of Cu(II) is given in Figure 3. It is quite clear that CBPF exhibited higher releasing capacity in the 5 g/L as shown in curve (b) than 2 g/L in curve (a). The longer washing time is, the more releasing content gets. The releasing test was the same with that of washing, but it had a different meaning. The antibacterial performance is implemented by the release of Cu(II). The reason for this fact may be that Cu(II) is desorbed to the protein in microorganism cell membrane, and then reacts with the functional groups of them such as amino group and sulfhydryl group. So the microorganism cell would be killed.

Morphology analysis

Three micrographs obtained accordingly from the untreated bamboo pulp fiber, the treated before washing and the treated after washing 300 min are shown in Figure 4. It can be seen from Figure 4(a) that the bamboo pulp fiber is made up of fibrils which is arranged along the length of the fiber basically. There are full of grooves between fibrils in the longitudinal fiber surface and apertures along the

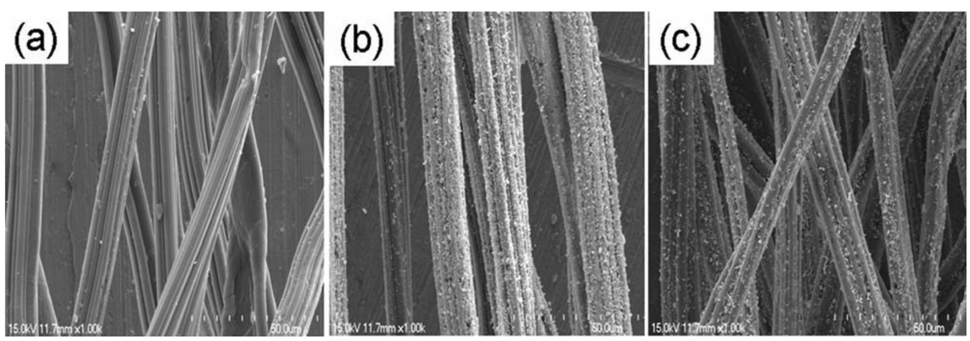

Figure 4 SEM microscopic images for (a) no Cu(II) treatment, (b) Cu(II) treated before washing, and (c) Cu(II) treated after 300 min washing.

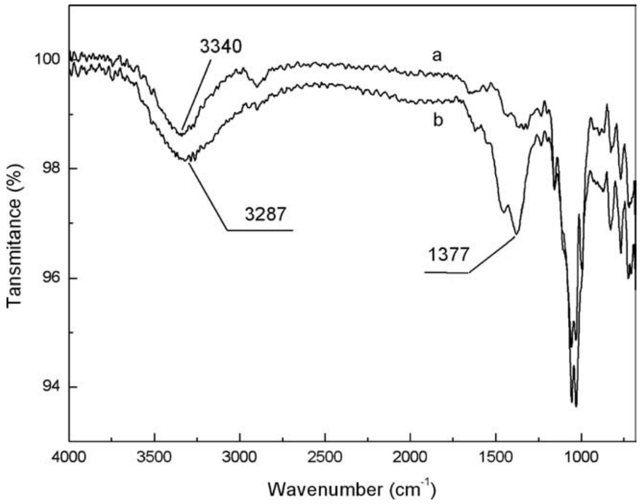

Figure 5 FTIR spectra of (a) bamboo pulp fabric and (b) CBPF; wavenumber (cm^{-1}) and transmittance (%).

length of the fibrils, and its morphology is straight stripes with a smooth, sleek shape.

However, compared with the untreated, the Cu(II) treated ones have a great different longitudinal surface morphology as shown in Figure 4(b,c). In Figure 4(b), the fiber longitudinal surface is densely covered by Cu(II) shaping a rough absorption stratum full of speckles on it. So there is almost no sign of grooves and apertures between fibrils. The smooth and sleek straight stripes become illegible. This is attributed to bamboo pulp fiber possessing a good absorption activity for Cu(II). In the same way, Figure 4(c) also represents the surface characteristics like in Figure 4(b), but there is a reduction in large extent. So it would be seen grooves and apertures by spells, Cu(II) speckles off and on and the fibril stripe outlines. This indicates that although washed 300 min, a lot of Cu(II) ions are immobilized in the fiber.

FTIR study

It would be seen from Figure 5 that FTIR spectra of bamboo pulp fabric and CBPF were similar except that an absorption band appeared at 1377 cm^{-1} or so, showing basically the characteristic spectra of cellulose. Both of them had a broad peak corresponding to —OH group stretching of cellulose observed in the range 3100–3500 cm^{-1} and another broad peak corresponding to —OH group in-plane bending of cellulose observed in the range 1300–1500 cm^{-1}. The two sharp peaks appears at 1058 cm^{-1} and 1032 cm^{-1} due to C—O stretching and a peak at 1158 cm^{-1} or so due to C—O—C asymmetric stretching. But the two bands around 1377 cm^{-1} (denoting —OH group bending) are distinguished by different absorptivity. The peak of CBPF is very stronger than that of bamboo pulp fabric, which should be attributed to the formation of intermolecular metal complex bond between Cu(II) and —OH group of cellulose in the bamboo pulp fiber.

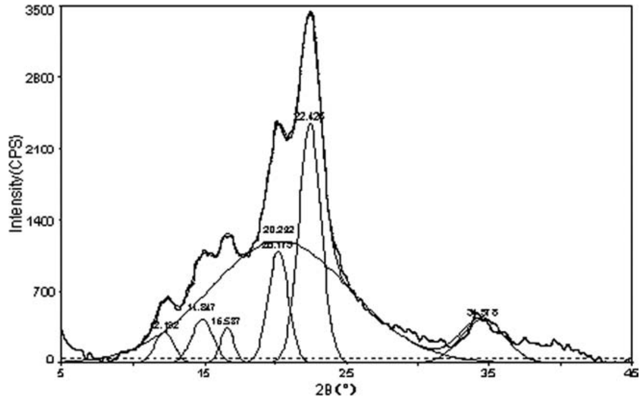

Figure 6 X-ray diffraction gram CBPF; 2θ (°) and intensity (CPS).

X-ray diffraction analysis

Figure 6 shows the XRD diffractograms of CBPF and it is very similitude with the untreated bamboo pulp fabric. The X-ray diffraction peaks were located near $2\theta = 12.2°$, 14.9°, 16.5°, 20.2°, 22.5°, and 35.2°. Generally, when native cellulose such as cotton fiber is regenerated after being dissolved in a suitable solvent or being treated in alkali solution, the cellulose I structure of the native cellulose is changed to the cellulose II structure. Bamboo pulp fiber was regenerated one, so it was the cellulose II structure.[4,20] In Figure 6, CBPF exhibited the characteristic peaks at $2\theta = 12.2°$ and 20.2°, respectively, attributed to the (110) and (002) planes of the typical cellulose II structure. So it is deduced that the cellulose crystal

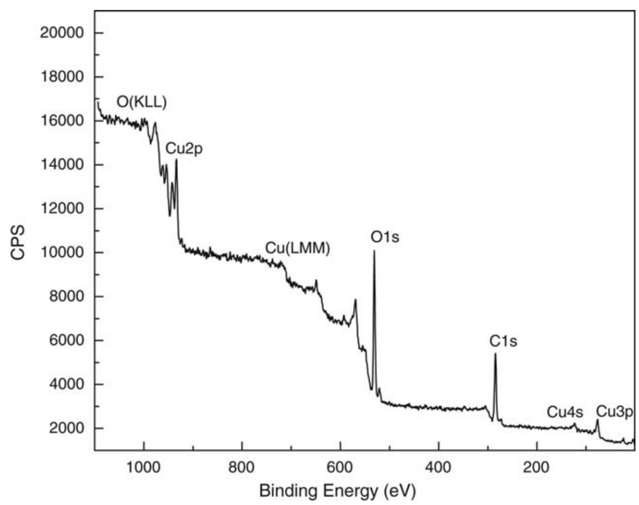

Figure 7 XPS spectra for CBPF; binding energy (eV) and CPS.

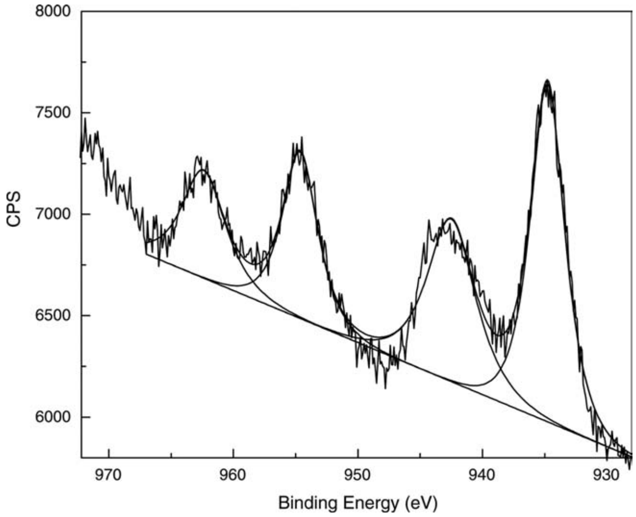

Figure 8 XPS spectra for Cu(II) in the surface of CBPF; binding energy (eV) and CPS.

structure of bamboo pulp fiber has not been changed in the processing of the Cu(II) treating.

But their crystallinity that was calculated by peak-fit method was changed.[18] The crystallinity of bamboo pulp fabric was 44.8% and that of CBPF decreases slightly to 40.5%. The reason may be that the copper liquor destroys cellulose fiber in crystal zone in a little extent.

XPS analysis

The X-ray photoelectron spectrum of CBPF is given in Figure 7. The element C, O, and Cu are displayed in it. The elemental composition of the CBPF was determined by XPS and the surface contents of C, O, and Cu were 53.70, 40.26, and 6.04 wt %, respectively.

The XPS spectra for $Cu2p_{3/2}$ from CBPF surface is shown in Figure 8. It exhibited a large band observed at about 934.7 eV binding energy, which corresponded to that type of $Cu(OH)_2$.[21,22] It is different from the structure type of CuO_4.[14] So it testified that Cu is 2^+ value and there is a coordinate bond between Cu(II) and two —OH groups of cellulose to form Cu(II) complex cellulose in according with FTIR.

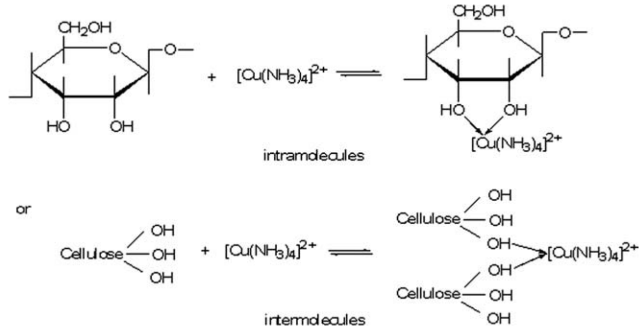

Figure 9 Chemical reactions in Cu(II) complex bamboo pulp fiber; intramolecules and intermolecules.

Although OH-2 and OH-3 are normally thought to be located above- and below-pyranose ring, respectively, it is possible for them to change into bath above- or below-pyranose via inversion of configuration. The —OH groups located on C_2 and C_3 of pyranose ring in cellulose fiber are ortho-position, so a chelate of five-membered ring may be formed by Cu(II) coordinated with them.[14] Chemical reactions in Cu(II) complex bamboo pulp fiber may be summed up mainly in the chemical equation as Figure 9.

Antibacterial performance

Table I shows surviving cells of *E. coli* and those of *S. aureus* in the bamboo pulp fabric and the cotton fabric individually. For *E. coli*, the count of surviving cells in the bamboo pulp fabric was 130,000 cfu/mL more than that of the cotton fabric. For *S. aureus*, the count of surviving cells in the bamboo pulp fabric was 420,000 cfu/mL less than that of the cotton fabric. Compared with the original count of surviving cells, there is no significant difference between them.

TABLE I
Cu (II) Antibacterial Property Against *S. aureus* and *E. coli*

	Escherichia coli		*Staphylococcus aureus*	
Bacterium	Surviving cells (cfu/mL)	Reduction (%)	Surviving cells (cfu/mL)	Reduction (%)
Cotton fabric	240,000	/	2,620,000	/
Bamboo pulp fabric sample	370,000	/	2,200,000	/
CBPF before washing	23,000	93.8	178,000	91.9
CBPF washing 300 min (5 g/L)	34,000	90.8	212,000	90.4

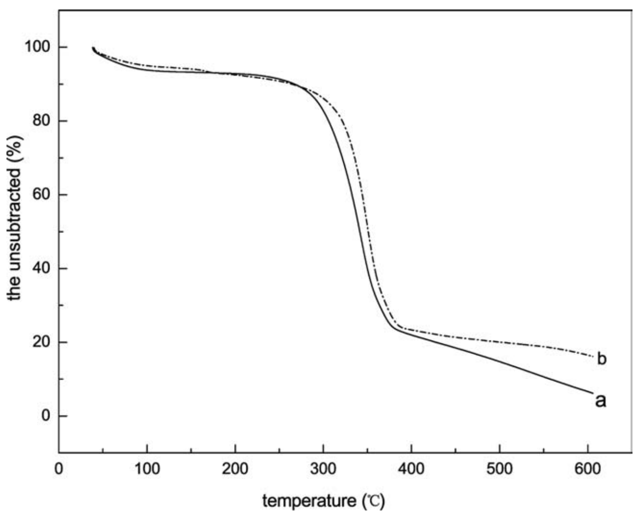

Figure 10 TG curves of the bamboo pulp fabric (a) and CBPF (b); Temperature (°C) and the unsubtracted (%).

Cotton fabric is known as no antibacterial activity, so bamboo pulp fabric would be deemed as no antibacterial activity too.

As stated in the Table I, Cu(II) expressed a better antimicrobial property owning to its antibacterial function. The results indicate that CBPF before washing shows high activities with 93.8% reduction against *E. coli* and 91.9% reduction against *S. aureus*. Even though after 300 min washing in 5 g/L detergent the Cu(II) content of CBPF was 1.8%(wt), it revealed high activity with over 90% reduction against *E. coli* and against *S. aureus,* cutting down very little. It is implied that the antimicrobial activity is not faded away in the procedure of washing.

TG analysis

Figure 10 illustrates the TGA curves of the bamboo pulp fabric (a) and CBPF (b). They could be distinctly divided into three stages.[1,23] The first stage was from 40°C to about 250°C. During this stage, the water and other residue solvent were vaporized and the weight loss was less than 10% for both of them. They are very similar in this stage. The second was from 250°C to ca. 390°C. During the stage, the crystalline region started to destruct and the cellulose simultaneously decomposed. It resulted in amorphous structure increased and the degree of polymerization decreased. For CBPF, it began to degrade at 305°C and completes at 385°C or so. By contrast, bamboo pulp fabric began to degrade rapidly at 285°C with the termination of degradation at ca. 375°C. The loss weights of CBPF and bamboo pulp fabric were around 73 and 75%, respectively. The last stage was that the crystalline region had been completely destructed and the cellulose decomposed totally from 375°C (385°C for CBPF) to the end of 600°C.

Although the TGA curves of CBPF and bamboo pulp fabric are similar in some way, the temperature of CBPF at the beginning and termination of degradation are higher than those of bamboo pulp fabric, so CBPF exhibits a better thermal stability.

Mechanical properties comparison

The mechanical properties of bamboo pulp fabric and CBPF are displayed in Figure 11. On the whole, there is no significant difference in breaking strength and breaking elongation between them. This is probably due to the two facts: first, because Cu(II) was bound with —OH group of cellulose to form network in CBPF, so it may increase breaking strength to some extent; second, the copper liquor in a lower concentration can dissolve cellulose fiber in both crystal zone and amorphous zone, and this may decrease breaking strength and increase breaking elongation in some way.

CONCLUSIONS

From this study, it is concluded that the bamboo pulp fabric just like cotton fabric has not possessed antimicrobial property. CBPF was formed after being

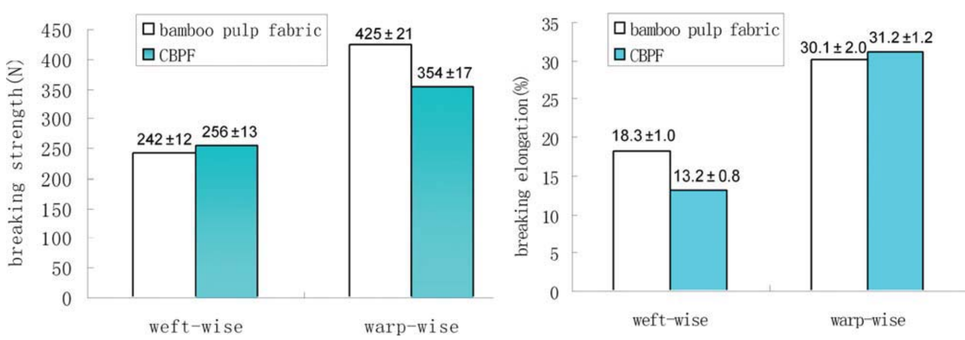

Figure 11 Mechanical properties of bamboo pulp fabric and CBPF of breaking strength (left) and breaking elongation (right); weft-wise, warp-wise; breaking strength (N), breaking elongation (%). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

treated in copper liquor, which is a novel antibacterial fabric with fair Cu(II) releasing capacity and an antibacterial property with reduction of 93.8% and 91.9% against *E. coli* and *S. aureus*, respectively.

From the analysis of structure, it can be deduced that a metal complex bond between Cu(II) and two —OH groups of cellulose was created in the type of Cu(OH-cellulose)$_2$. The crystallinity of CBPF decreased slightly, but the typical cellulose II structure was not changed. It is manifested by the fact that CBPF has a better thermal stability than bamboo pulp fabric. In addition, CBPF's mechanical properties were not changed very much. This implies that CBPF may find potential applications in textile and medical industry.

References

1. Yang, Z.; Xu, S.; Ma, X.; Wang, S. Wood Sci Technol 2008, 42, 621.
2. Deshpande, A. P.; Bhaskar Rao, M.; Lakshmana Rao, C. J Appl Polym Sci 2000, 76, 83.
3. He, J.; Cui, S.; Wang, S.-Y. J Appl Polym Sci 2008, 107, 1029.
4. Wang, Y.-P.; Gao, X.-S. Plant Fiber Sci Cha 2006, 28, 97 (in Chinese).
5. Liu, G.-P.; Wang, R.; Li, R.-Z.; Wang, Y.-Q. Wool Text J 2004, 11, 41 (in Chinese).
6. Mary, G.; Bajpai, S. K.; Chand, N. J Appl Polym Sci 2009, 113, 757.
7. Son, W. K.; Youk, J. H.; Lee, T. S.; Park, W. H. Macromol Rapid Commun 2004, 25, 1632.
8. Sachinvala, N.; Parikh, D. V.; Sawhney, P.; Chang, S.; Mirzawa, J.; Jarrett, W.; Joiner, B. Polym Adv Technol 2007, 18, 620.
9. Sharma, R.; Agarwal, S. K.; Rawat, S.; Nagar, M. Transition Met Chem 2006, 31, 201.
10. Jeewoth, T.; Bhowon, M. G.; Wah, H. L. K. Transition Met Chem 1999, 24, 445.
11. Anacona, J. R.; Bastardo, E.; Camus, J. Transition Met Chem 1999, 24, 478.
12. Sau, D. K.; Butcher, R. J.; Chaudhuri, S.; Saha, N. Mol Cell Biochem 2003, 253, 21.
13. Takenaka, S.; Ihara, T.; Takagi, M. J Mol Recognit 1990, 3, 156.
14. Chen, W.; Shen, Z. Q.; Liu, G.; Shirai, H. Acta Polym Sinica (China) 1998, 3, 431.
15. Miyamoto, I.; Inamoto, M.; Matsui, T.; Saito, M.; Okajima, K. Polym J 1995, 27, 1113.
16. Tapeiro, H.; Townsend, D. M.; Tew, K. D. Biomed Pharmacother 2003, 57, 386.
17. FZ/T 73023–2006. Antibacterial knitwear, China.
18. Lu, Y.-H.; Lin, H.; Chen, Y.-Y.; Wang, C.; Hua, Y. R. Fiber Polym 2007, 8, 1.
19. Chou, W.-L.; Yu, D.-G.; Yang, M.-C. Polym Adv Technol 2005, 16, 600.
20. Han, S. O.; Son, W. K.; Youk, J. H.; Park, W. H. J Appl Polym Sci 2008, 107, 1954.
21. Barr, T. L. J Vac Sci Technol A 1991, 9, 1793.
22. Barr, T. L. J Phys Chem 1978, 82, 1801.
23. Peng, S.; Shao, H.; Hu, X. J Appl Polym Sci 2003, 90, 1941.