

Structure and Properties of Silk Fibroin Modified Cotton

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Abstract: In this research, a novel cotton fiber with a silk fibroin (SF) coating was prepared by the oxidation of a cotton thread with sodium periodate and subsequent treatment in a solution of silk fibroin. The structures of both the oxidized cotton samples and the SF modified cotton samples were investigated by Fourier transform infrared (FT-IR) in combination with X-ray photoelectron spectroscopy (XPS) analysis. Other performances such as surface morphology and breaking strength were also studied. The results indicated that the weight of the oxidized cotton samples increased during SF treatment, while that of the un-oxidized cotton (pure cotton) samples reduced after SF treatment. Compared with the pure cotton samples, the oxidized cotton clearly showed a characteristic absorption band at 1730 cm^{-1} due to the stretching vibration of the C=O double bond of the aldehyde group. After being treated with the SF solution, the oxidized cotton fiber showed a weakened characteristic absorption band at 1730 cm^{-1} and a new absorption band at round 1540 cm^{-1} , suggesting the formation of C-N bond between aldehyde groups in the oxidized cotton and primary amines in the silk fibroin. The results were also confirmed by XPS analysis. Compared with the oxidized cotton samples, the SF treated cottons had relatively smooth surfaces, similar breaking strength, and the improved wrinkle recovery angles. The results in this research suggest that cotton based materials with protein coating can be achieved without using any other crosslinking agents by the method introduced.

Keywords: Cotton, Oxidation, Sodium periodate, Silk fibroin

Introduction

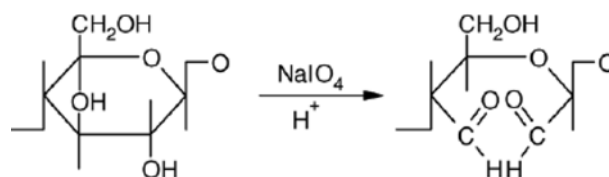
Cotton, one of the most important natural textiles, contains mainly cellulose of high molecular weight ranging from 2.5×10^5 to 1×10^6 or more [1]. It is a polymer with glucose linked through 1,4- β -glucosidic bond and is widely used in clothing fields due to its excellent characteristics including regeneration, bio-degradation, softness, affinity to skin, and hygroscopic property. Recently, many studies have been devoted to the preparation, modification, and application of cellulose and its derivatives [2-5]. Oxidation, as a new modification method to cellulose, aroused many researchers' interest and enthusiasm. They have carried out a series of experiments on the oxidation of cellulose by periodic acid and its salts. Among them, partial oxidation of cellulose leads to polymers having various functional groups (e.g. aldehyde and carboxyl groups) in addition to the primary and secondary hydroxyl groups, which broadens the range of applications of cellulose, as well as cotton fibers [6-8].

Oxidation of cellulose causes changes in the structure and crystallinity of the resulting molecules, and it will affect its chemical and physical properties. Thus previous researches mainly focused on the analysis of their fine structure [7,9-11]. Meanwhile, oxidized cotton has been widely applied to medical fields, for example the development of absorbable surgical suture. However, less attention has been paid to the oxidized cotton fiber for the textile usage [12,13].

Silk fibroin (SF) is a natural biological polymer composed of 18 α -amino acids, among which Gly, Ala, and Ser are the main amino acids [14,15]. Silk fibroin can be obtained by removing the outer sericin of silk fibers by treating them in

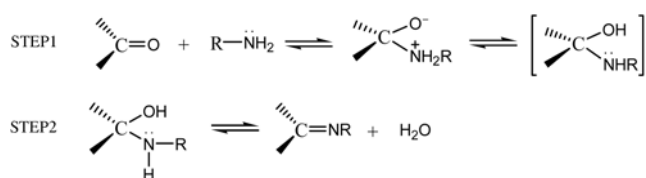
anhydrous sodium carbonate solution at an appropriate temperature. Silk fibroin has been extensively utilized in the production of fabrics and art works for centuries due to its unique gloss, handle, and mechanical properties [15]. Besides these applications, fibroin proteins have found an effective application as an ingredient in cosmetic formulations including skin and hair care products due to their moisturizing effect. Therefore, in recent years, the range of possible end-users of fibroin has considerably expanded with emphasis on its use as finishing agent for natural or man-made textiles requiring properties of moisture absorption, antistatic properties, softness, and comfort.

Previously, we had briefly reported on the structure and mechanical properties of cotton fiber oxidized by sodium periodate [16]. In this study, cotton fiber was firstly oxidized by sodium periodate to yield a product with 2,3-dialdehyde units along the cotton chain [8,10,11,17] (termed "oxidized cotton fiber" below) (Scheme 1) [18]. Then the oxidized cotton fibers were treated in silk fibroin (termed "SF") solution to get SF modified cotton fiber. The present study took advantage of the active aldehyde group in oxidized cotton samples and coated silk fibroin onto cotton samples leading to improved physical or mechanical properties. We expected that the oxidized cotton fiber could be combined with silk fibroin molecule without any other reagents [19],



Scheme 1. Oxidation of cotton fiber to 2,3-dialdehyde cellulose.

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Scheme 2. The reaction between 2, 3-dialdehyde cellulose and SF.

and the reaction mechanism between oxidized cotton and SF is shown in Scheme 2.

Experimental

Materials

Cotton yarns scoured and bleached (called untreated cotton) as well as cotton fabrics were purchased from Suzhou Hongxiang printing & dyeing factory. *Bombyx mori* (*B. mori*) silk was commercially obtained from China Import & Export. All chemicals (sodium carbonate, sodium periodate (NaIO_4 , 99.8%), glycerol, HCl, NaOH, ethanol, and calcium chloride) used for the following investigations were of analytical grade. Deionized water was used throughout the work.

Preparation of SF Powder

Raw *B. mori* silk was first degummed twice in the boiling solution containing 2 g/l Na_2CO_3 and 10 g/l degumming agent in liquor ratio of 1:100 for 1 h in order to remove the sericin protein [20]. Then the resulting degummed fiber was dissolved in a solution of calcium chloride, ethanol, and water (CaCl_2 : $\text{C}_2\text{H}_5\text{OH}$: H_2O : 1:2:8 mole ratio) at 60 °C for 30 min. After filtering, the silk fibroin-salt solution was dialyzed for 3 days against running pure water to remove CaCl_2 , smaller molecules, and some impurities using a membrane, and then the solution was freeze-dried. Finally, the SF powder with the molecular weight of 5000-30000 (Mw) was obtained by the degradation with HCl as the method in reference [21].

Preparation of Oxidized Cotton Fiber by Periodate Oxidation

Cotton fibers were subjected to a mild oxidation process that selectively modifies the C2 and C3 positions in the cellulose chain in the following way. To investigate the cotton behavior at different level of oxidation, the cotton samples were treated with different solutions of sodium periodate (1.5 g/l NaIO_4 , 10.7 g/l NaIO_4 , 21.4 g/l NaIO_4) for different treatment times. The ratio of sample/solution was 1:100. The samples were immersed in a closed vessel with the sodium periodate solution and the mixture was oscillated gently at room temperature in the dark. At the end of the oxidation processes, the samples were immersed in the 0.1 M glycerol aqueous solution for 0.5 h to remove un-reacted oxidant, and were washed with deionized water up to neutral conditions (pH 7). At last the samples were soaked in deionized water

for 24 h at ambient temperature and then were dried in air.

Preparation of SF Treated Cotton Fiber

SF solution was prepared with deionized water. The pH value of the SF solution was adjusted to 6.0 by 0.1 M HCl. Then the above mentioned oxidized cotton samples were immersed in a SF solution (range from 5 g/l to 20 g/l) for 1 h at 60 °C, and then padded at 90 % wet pick-up. After that, the samples were cured in a laboratory oven at 170 °C for 3 min. The treated samples were washed with tap water and soaked in deionized water for 24 h at ambient temperature. The SF treated cotton samples were dried at 80 °C for 2 h to produce the modified cotton threads.

For comparison, the un-oxidized cotton samples (termed pure cotton) were also treated according to the above process.

Weight Change Percentage Test

The samples untreated or treated with SF solution conditioned in a constant temperature of 20 °C and a constant humidity of 65 % were weighed on a BS210S photoelectric scale. The change percentage of weight for the samples during the SF treatment was calculated as following:

$$W_c(\%) = \frac{W_2 - W_1}{W_1} \times 100$$

where W_1 and W_2 represent the weight of sample before and after SF solution treatment, respectively. If W_c is positive, it means weight gain occurring during the treatment, otherwise weight loss.

Scanning Electron Microscopic (SEM) Analysis

Microstructural surface morphology of samples was observed by Model S-570 scanning electron microscope. The samples were gold sputtered to give the samples electronic conductivity under a vacuum prior to the observation.

FT-IR Spectroscopy

Infrared spectra were recorded on a Nicolet 5700 FT-IR spectrophotometer using the traditional transmission technique for KBr pellets. KBr pellets of samples were prepared by mixing 1.5-2.0 mg of cotton powder with 200 mg KBr (spectroscopic spectroscopic grade) in a vibratory ball mixer for 20 s. The round pellets were prepared with a standard device under a pressure of 30 Mpa. IR spectra were recorded at 4 cm^{-1} resolution and 64 scans were taken for each sample. The measurements were performed at 20 °C and a relative humidity of 65 %.

XRD Patterns

XRD patterns of cotton powder samples were obtained with a model D/MAX3C X-ray diffraction system at voltage of 40 kV, current of 30 mA, and scan rate of 2°/min. The crystallinity of the cotton fiber was calculated by the method of peak separation and *Gaussian* peak fit with the software

of peakfit v 4.12 [20]. The formula is as followed:

$$X_c(\%) = \frac{I_c}{I_c + I_a} \times 100$$

where X_c is the crystallinity of the cotton fiber, I_c is the sum of all crystal diffraction peak intensities, and I_a is the diffraction intensity of amorphous peak.

XPS Analysis

XPS spectra were recorded with 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. In general, the X-ray anode was run at 180 W and the high voltage was kept at 12.0 kV. The position of the carbon peak (284.8 eV) for C1s was used to calibrate the XPS scale for all substrates. XPS data fitting was performed using commercially available software with 100 % Gaussian curve fitting. A linear background subtraction was used for C1s, N1s, and O1s curves, and a Shirley background subtraction was used for Cu 2p3/2 (932.67 eV).

Determination of Breaking Load and Elongation

The breaking strength and breaking elongation of cotton yarn samples were determined at an effective gauge length of 250 mm and extension rate of 250 mm/min performed on a YG020 electron single strand meter. The samples were conditioned in the room (20 °C, a relative humidity of 65 %) for 48 h before measurement. The results were averaged with 20 samples.

Wrinkle-resistant Properties

The dry wrinkle-recovery angles of the silk fabric samples were evaluated according to AATCC Test Method 66-1998 using YG541A wrinkle-recovery tester. The results were averaged with 10 warp and 10 weft samples, respectively.

Results and Discussion

Weight Change of SF Treated Cotton Fiber

The oxidized cotton yarns (1.5 g/l $NaIO_4$) and the pure cotton yarns were treated with SF solution of different concentrations ranging from 5 g/l to 20 g/l and their weights before and after the treatment were investigated (see Figure 1). Weight loss can be observed for the pure cotton samples during SF treatment, while weight gain for the oxidized ones. The weak parts of cotton fibers were eroded by the weak acidity of SF solution, consequently the weight of pure cotton yarns decreased during the SF treatment. As for the oxidized samples, in addition to the erosion on fibers by the SF solution, we believe that the crosslinking reaction between SF and the oxidized cotton fibers occurred. Meanwhile, more SF could be coated onto the rough surface of oxidized cotton fiber via physical absorption. Due to the above

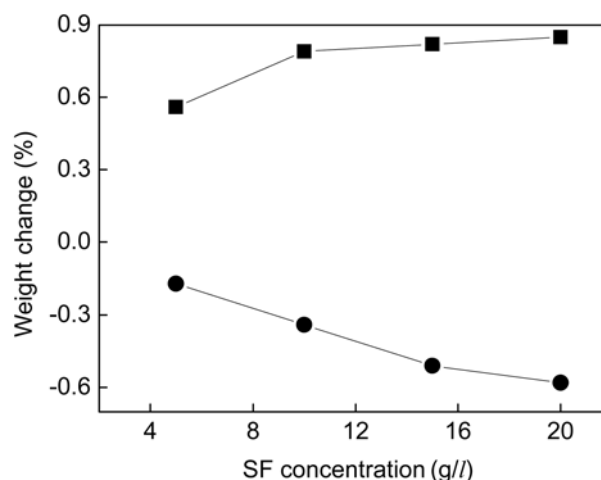


Figure 1. Weight change percentage of cotton samples: ■ represents the SF treated oxidized cotton and ● represents the SF treated un-oxidized cotton.

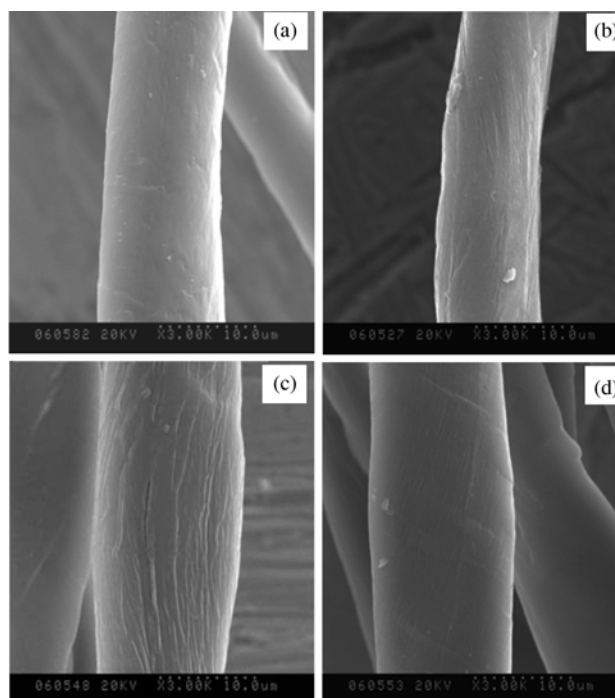


Figure 2. SEM photomicrographs of (a) the pure cotton fiber, (b) the SF treated cotton fiber, (c) the oxidized cotton fiber ($NaIO_4$ 21.4 g/l at 40 °C for 5 h), and (d) the SF treated oxidized cotton fiber ($NaIO_4$ 21.4 g/l at 40 °C for 5 h).

actions of SF solution, the weight of the oxidized samples increased.

Scanning Electron Microscopic Analysis

The surfaces of the cotton fibers before and after SF solution treatment were morphologically observed by SEM. The surface of the pure cotton fiber shown in Figure 2(a)

was smooth, while erosion stripes appeared on the surface if it was treated with SF solution. In Figure 2(c), long and deep stripes were found on the surface of the oxidized cotton fiber, which is attributed to that the amorphous cellulose near the surface of the microfibril was removed. Surprisingly, when the oxidized cotton fiber treated with SF solution, the surface turned out to be smooth again. It illustrates that the SF treatment can modify the surface properties of cotton fibers, especially the oxidized cotton fibers.

FT-IR Spectra of Oxidized Cotton Fiber

Figure 3 shows the FT-IR spectra of the pure cotton and the cotton oxidized with sodium periodate of different concentrations. Curve a is the spectrum curve of the pure cotton fiber. We observed a broad peak centred at 3300 cm^{-1} corresponding to O-H stretching, and a broad peak at $3000\text{--}2800\text{ cm}^{-1}$ region for C-H stretching. Although cotton fiber has $\text{-CH}_2\text{-}$ groups in their molecular chains, the peaks corresponding to the symmetric and asymmetric stretching modes have never been separated as sharp peaks. In addition, a peak around 1640 cm^{-1} was due to the adsorbed water molecules [22]. Compared with curve a, a new characteristic absorption band of the oxidized cellulose clearly appeared at around 1730 cm^{-1} due to the stretching vibration of the C=O double bond of the aldehyde group in curve b and curve c. The intensity of the peak at 1730 cm^{-1} enhanced gradually with the increasing concentration of oxidant as well as the peak at 880 cm^{-1} assigned to the formation of hemiacetal bonds between the aldehyde groups and the neighbor hydroxyl groups. Meanwhile, peaks at 1060.2 cm^{-1} (OH distortion vibration), 1235.6 cm^{-1} (OH in-plane bending), 1282.2 cm^{-1} (CH deformation stretch vibration), 1164.8 cm^{-1} (asymmetry bridge bond COC stretch vibration), and $700\text{--}500\text{ cm}^{-1}$ (CC

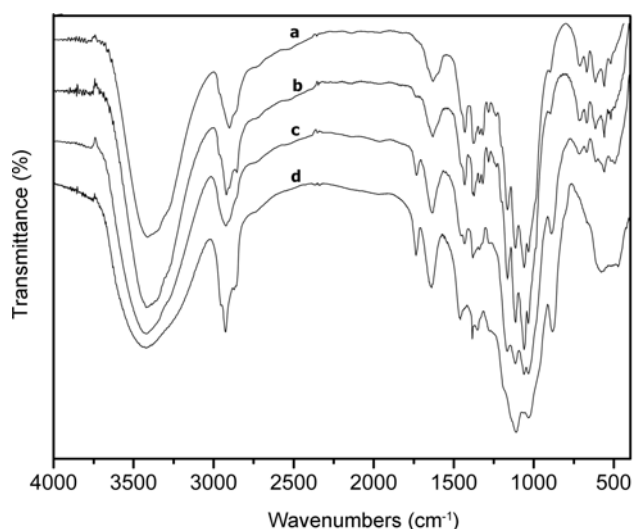


Figure 3. IR spectra of the oxidized cotton samples; (a) untreated, (b) oxidized by 1.5 g/l NaIO_4 at 40 °C for 1 h, (c) oxidized by 10.7 g/l NaIO_4 at 40 °C for 5 h, and (d) oxidized by 21.4 g/l NaIO_4 at room temperature for 240 h.

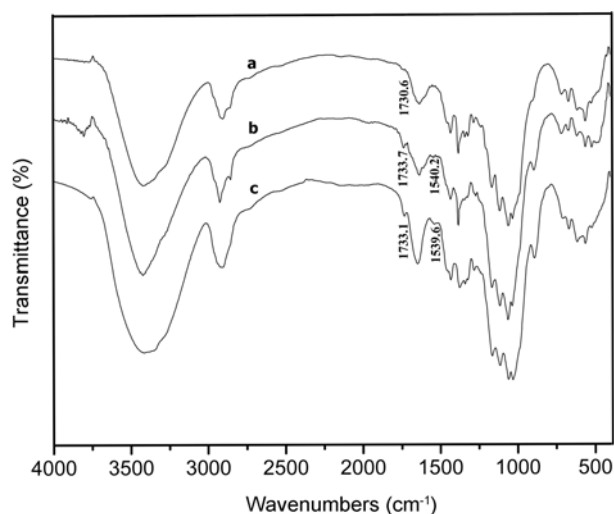


Figure 4. IR spectra of the oxidized cotton fiber treated with SF solution; (a) 1.5 g/l NaIO_4 oxidized at 40 °C for 1 h, (b) 10.7 g/l NaIO_4 oxidized at 40 °C for 5 h, and (c) 21.4 g/l NaIO_4 oxidized at 40 °C for 5 h.

stretch vibration) became weak. It illustrates that the cotton macromolecule decomposed partly during the oxidation by sodium periodate [18].

FT-IR spectra of the oxidized cotton fiber treated with SF solution were shown in Figure 4. A new peak at 1540 cm^{-1} appeared and the intensity was strengthened with the increasing oxidant concentration after the SF treatment. It displays that CN bond formed between the aldehyde group and the silk fibroin. As for the low-oxidized sample, the peak at 1540 cm^{-1} was not obvious (see Figure 4(a)). This can be explained in this way: the number of aldehyde group was smaller as compared with the high-oxidized cotton samples, so the new CN bond was too little to be detected by FT-IR. In Figure 4, the peak at 1730 cm^{-1} can still be observed for the SF treated oxidized samples, but the intensity of the peak was weakened as compared with that of the corresponding oxidized sample before SF treatment. One reason was that the reaction between SF solution and the oxidized cotton fiber was not a homogeneous reaction and thus the silk fibroin molecules were not able to penetrate into the inner part of cotton fiber easily. The other reason was that the aldehyde groups were close to the glucose and stereospecific blockade existed when reacting with SF, so only part of aldehyde groups took part in the reaction.

XRD Patterns of Cotton Fiber

Figure 5 shows the XRD curves for the oxidized cotton samples before and after SF solution treatment. For all the samples, the peaks were located near $2\theta=14.8, 16.6, 22.9,$ and 34.5 ° , which were the characteristic positions of $101, 10\bar{1}, 002,$ and 040 reflections of cellulose I, respectively [23]. This, together with the relative peak intensities in each spectrum, indicates that these cotton fibers exhibited

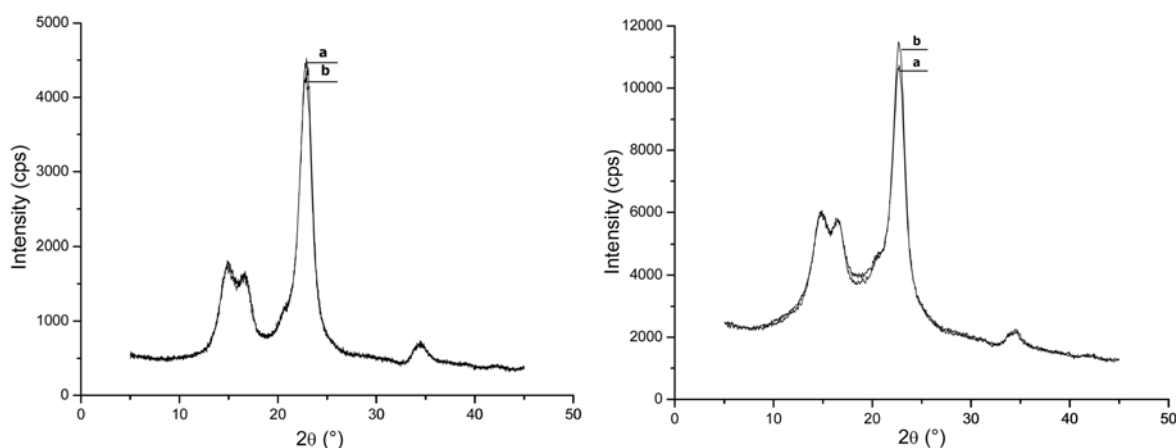


Figure 5. XRD curves of the oxidized cotton fiber before (marked a) and after (marked b) SF solution treatment. The left is for the samples oxidized with 1.5 g/l NaIO₄ at 40 °C for 1 h and the right is for the samples with 21.4 g/l NaIO₄ at 40 °C for 5 h.

Table 1. Crystallinity of the oxidized cotton samples before and after SF solution treatment (%)

Samples	1.5 g/l NaIO ₄	21.4 g/l NaIO ₄
Oxidized cotton fiber	69.99	47.67
SF treated oxidized cotton fiber	69.88	54.63

cellulose I crystalline structure. Their crystallinities calculated by peakfit method are shown in Table 1. As compared with that of the pure cotton fiber (68.66 %), the crystallinity of the cotton fiber oxidized in 1.5 g/l NaIO₄ solution changed little, while decreased greatly to 47.67 % in 21.4 g/l NaIO₄ solution. This can be explained that under low oxidation degree only weak parts were eroded away and small amount of hydroxyl group was oxidized into aldehyde group, while with high oxidation degree, the cleavage of the C₂-C₃ bond of glucopyranoside ring occurred and the molecular chain decomposed partially during the sodium periodate oxidation process. From Table 1, it can also be drawn that the crystallinity of the oxidized samples at high level oxidation (21.4 g/l NaIO₄) after SF solution treatment increased 6.56 %. The reason was that part of crystalline region of the cotton fiber transformed into amorphous region during oxidation. This provided more chances for silk fibroin to react with active group in the cotton fibers and then more covalent groups were formed between them. The other reason was that the intensity of hydrogen bond among molecules was enhanced during the SF treatment. On the other hand, for the samples with low level oxidation (1.5 g/l NaIO₄), the crystallinity changed little after SF solution treatment. This can be explained in this way: only small quantity of covalent bonds were formed between oxidized cotton and SF, and the reaction mainly occurred on the surface of cotton fiber.

XPS Analysis

The chemical composition of the cotton fiber surfaces was

determined by X-ray photoelectron spectroscopy (XPS). XPS has been extensively used for the analysis of the composition of the outermost surface layers (analysis depth of a few nanometres) of fibers to our knowledge. The chemical shifts of carbon (C1s) in cotton fibers can usually be easily classified into four categories: unoxidized carbon (C-C), carbon with one oxygen bond (C-O), carbon with two oxygen bonds (O-C-O or C=O), and carbon with three oxygen bonds (O=C-O [24]).

The relative amounts of carbons with different number bonds to oxygen were determined from carbon C1s spectra using peak-fitting into three symmetric Gaussian components. Both the relative peak positions and relative peak widths were fixed in the curve fitting process. The C1s peak of pure cotton sample was deconvoluted into three sub-peaks. The sub-peaks at 284.76 eV, 286.04 eV and 287.65 eV are contributed to C-C or C-H, C-O, and O-C-O, respectively (Figure 6(a)) [25]. The sub-peak of O-C-O was shifted from 287.65 eV to 288.23 eV after oxidation with sodium periodate, which is contributed to C=O group (Figure 6(b)). Meanwhile, the area of the peak belonging to C-O group at round 286.0 eV was reduced from 20.72 % (before oxidation) to 17.17 %. All these results indicate that the dialdehyde cellulose was gained from the cotton fiber by oxidized with sodium periodate.

The C1s XPS spectra of the oxidized cotton sample after treating with SF solution are presented in Figure 6(c). Compared with that of the oxidized cotton fiber (Figure 6(b)), a new sub-peak at binding energy of 287.24 eV attributed to C-N bond was observed. In addition, SF treatment also produces an obvious effect on the carbon (1s) XPS spectrum, where a reduction in the spectral contribution of the 288.0 eV component, from approximately 17.17 % in the oxidized cotton to 6.45 % in the SF modified cotton fiber, is apparent. This can be explained with the fact that only part of the aldehyde groups in the oxidized cotton sample reacted with

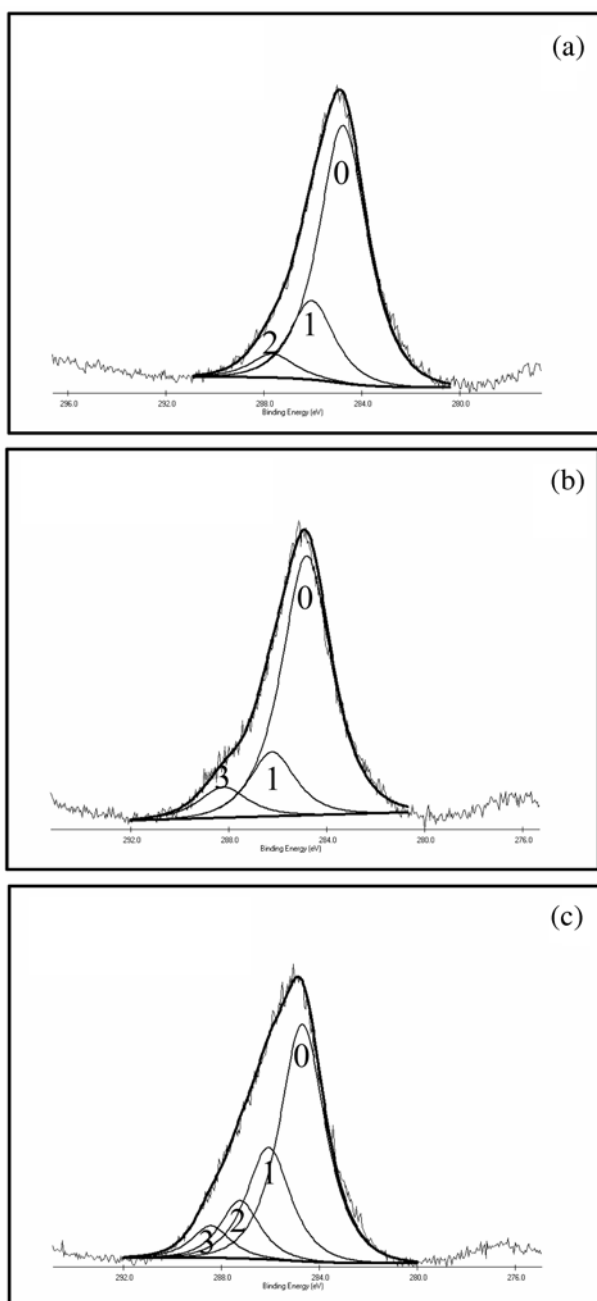


Figure 6. XPS spectra of C1s peaks for the followed cotton samples; (a) the pure cotton fiber, (b) the oxidized cotton fiber, and (c) the SF treated oxidized cotton fiber.

SF, which was in accordance with the results obtained from spectra of FT-IR.

It can also be observed that the N1s XPS spectra of SF powder only have one sub-peak at 399.62 eV, while that of the SF treated oxidized cotton sample have two sub-peaks (Figure 7). It implies that the nitrogen binding mode of SF on the surface of the oxidized cotton samples changed compared with that of the pure SF powder.

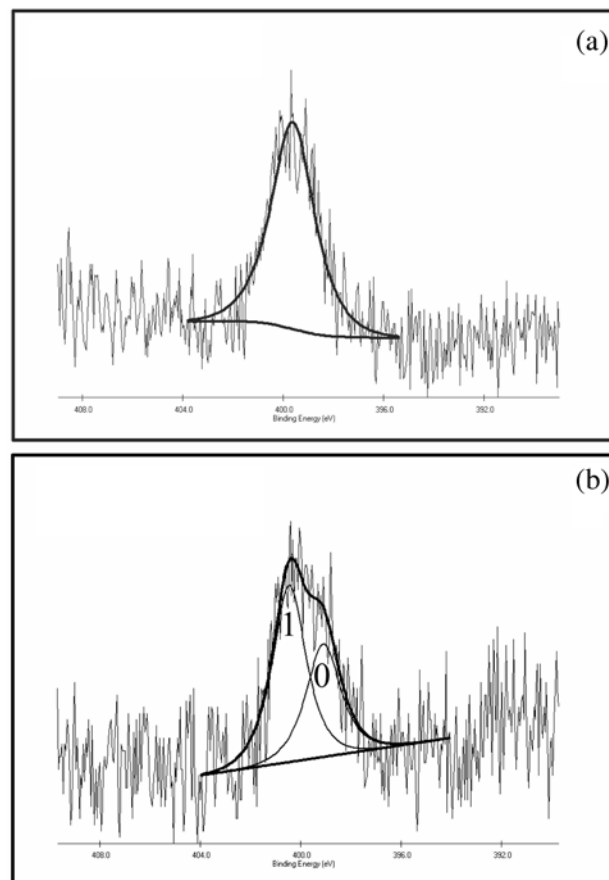


Figure 7. XPS spectra of N1s peaks for; (a) the SF powder and (b) the SF treated oxidized cotton sample.

The only atoms analyzed by XPS in pure cellulosic fibers are carbon and oxygen, since hydrogen cannot be detected due to the technique limitation. Figure 8 shows the wide scan spectra of the oxidized cotton sample before and after SF treatment. No new element was introduced to the pure cotton fiber when it was oxidized with sodium periodate. As expected, the main elements of the oxidized cotton fiber detected were carbon and oxygen. In other hand, for the SF treated oxidized cotton sample, nitrogen element was detected. XPS results reconfirmed the formation of covalent groups between cotton and SF as seen from FTIR. Conclusively, SF had been coated onto the surface of cotton fibers.

Breaking Strength and Elongation

Figure 9 shows the breaking strength and the breaking elongation of different level oxidized cotton samples before and after treating with SF solution. As compared with the oxidized cotton sample, no difference was observed of the SF treated oxidized cotton sample for the mechanical parameters of breaking strength and breaking elongation. That is to say, the effect on the oxidized cotton sample by the treatment of SF solution was relatively negligible. The

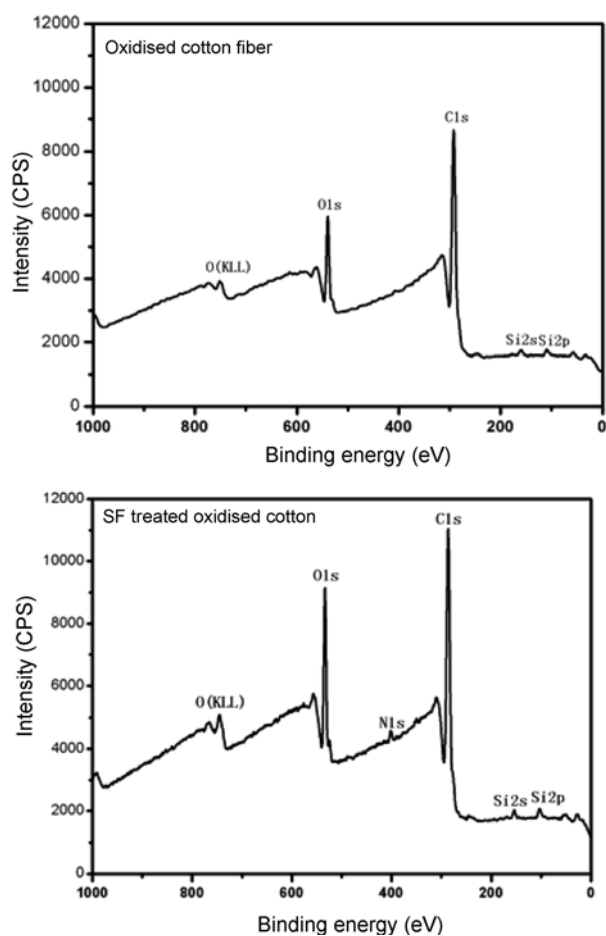


Figure 8. Wide scan spectra of the oxidized cotton sample before and after SF treatment.

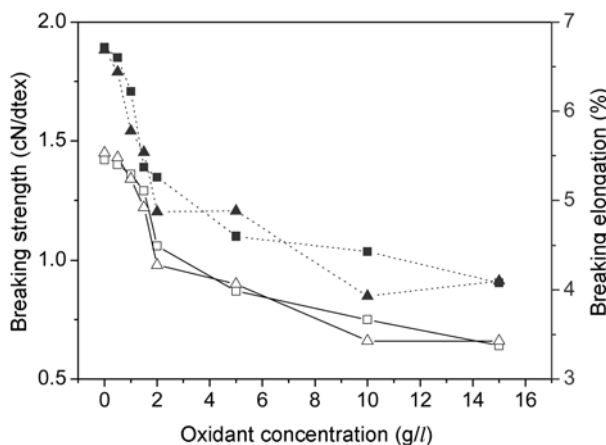


Figure 9. Tensile strength and elongation of the oxidized cotton sample before (square) and after (triangle) SF solution treatment. Hollow pattern represents breaking strength and solid centre pattern represents breaking elongation.

breaking strength and elongation were only related to the oxidation degree, which reduced the breaking strength and elongation dramatically. So as for the usage for garment, the

Table 2. Wrinkle recovery angles of the treated cotton fabrics

Samples	Immediate-wrinkle recovery angle (°) (W+F)	Delay-wrinkle recovery angle (°) (W+F)
Pure cotton fabrics	101	109
SF treated oxidized cotton fabrics	179	198

oxidation condition should be investigated further in future to get a reasonable oxidation process.

Wrinkle-resistant Properties of SF Treated Oxidized Cotton Fabrics

The immediate-elastic deformation and delayed-elastic deformation of the cotton samples before and after SF solution treatment is shown in Table 2. The wrinkle recovery angle of the cotton samples increased a lot when they were treated by sodium periodate solution in combination with SF solution. That is to say, the SF treated oxidized cotton samples have a good anti-crease property.

Conclusion

Silk fibroin coated cotton can be prepared successfully by oxidizing cotton with sodium periodate and subsequently treated with silk fibroin solution. Periodate oxidized cotton exhibits two characteristic FTIR bands at near 1730 cm^{-1} and 880 cm^{-1} , and the intensity of the two peaks enhanced with the increasing degree of oxidation. After the oxidized cotton samples treated with SF solution, the characteristic absorption band at 1730 cm^{-1} weakened and a new peak at 1540 cm^{-1} appeared suggesting new bond (C-N) formed between the cotton fiber and the silk fibroin, which was also confirmed by XPS spectra. The weight of the oxidized cotton sample increased and its surface got smooth after silk fibroin solution treatment. At high level oxidation, the crystallinity of the sample decreased, and then improved after SF solution treatment. However, at low level oxidation, oxidation or SF treatment, the crystallinity of samples changed little. The breaking strength and elongation of the oxidized cotton sample changed little before and after SF solution. That is to say, the treatment of SF solution has no negative effect on the tensile properties of the oxidized cotton samples. Moreover, the crease resistance property of the SF treated oxidized cotton samples improved and their surfaces have the property of protein.

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