Improving the Antibacterial and UV-Resistant Properties of Cotton by the Titanium Hydrosol Treatment

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ABSTRACT: The titanium hydrosol was prepared and treated on the cotton fabrics to improve its antibacterial and UV-resistant properties. The sol size and gel morphology on the fabric were characterized by Nanosizer, SEM, and AFM. The antibacterial reduction rate of the treated fabrics against *Staphylococcus aureus* and *Escherichia coli* reached above 95%, and the corresponding UV transmittance value of the treated fabrics decreased considerably, with a ultraviolet protection factor of 50 or excellent grade, and the protection was tested according to the Australian/New Zealand standards. In spite of 50 washing cycles, the antibacterial and UV-resistant properties changed almost little because of the strong affinity between the gel particles and cellulose material. The strength tests of the treated fabrics also showed no negative effects from the treatment on the fabrics. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 1478–1482, 2006

Key words: titanium hydrosol; sol–gel; antibacterial; UV-resistant; coating; fibers

INTRODUCTION

The sol–gel processes based on the hydrolysis and condensation of metal alkoxide compounds have various technical applications, such as the preparation of special glass, ceramic, and coatings.[1–3] The basic kinetics of the processes can be well described as both hydrolysis and polycondensation reactions, shown as the eqs. (1)–(3).[4]

$$M(OR)_x + H_2O \rightarrow M(OR)_{x-1}OH + ROH \quad (1)$$

$$2M(OR)_{x-1}OH \rightarrow (OR)_{x-1}M{-}O{-}M(OR)_{x-1} + H_2O \quad (2)$$

$$M(OR)_{x-1}OH + ROH \rightarrow (OR)_{x-1}M{-}OR + H_2O \quad (3)$$

Where M is a metal species (Ti, Si, Al, Zr, etc.), and R is an alkyl group (methyl, butyl, ethyl, etc.). These reactions generate an oxide skeleton in the solution. Upon exposure to the atmosphere or heating, the solution gels and becomes rigid.

In the recent years, the sol–gel technology has been involved in the applications on textiles, and the fabrics are modified chemically to impart the durable press, water-repellent, hydrophilic, hydrophobic, antistatic properties, etc.,[5–9] whereas there is less report on the antibacterial and UV-resistant properties of the sol–gel treated fabric. So, we did further research on the sol–gel application in the textile function.

In this article, the titanium hydrosol was prepared using tetrabutyl titanate as the precursor with hydrochloric acid, acetic acid, and water to improve the antibacterial and UV-resistant properties of cotton fabrics. When the fabric was treated with the titanium hydrosol by traditional pad-dry-cure process, the nanogel particles link together with interconnected Ti—O—Ti bonds to form inorganic network on the fabric. The formed titanium gel particles can strongly absorb the ultraviolet rays so that the antibacterial and UV-resistant properties both are markedly enhanced, because there is a certain relation between the absorption intensity of UV radiation and the activity of the photocatalysis. The stronger the UV-absorption intensity, the higher the activity, where the strong absorption intensity implied that more electrons could be promoted from the valence band into the conduction band and more separate electrons or holes could be produced, which will help to enhance the photocatalytic activity to kill the bacteria.

EXPERIMENTAL

Materials

Scoured and bleached cotton woven fabric (140 g/m^2) was obtained from Shanghai No.1 Dyeing Factory. The used reagents were of analytical grade as the following: tetrabutyl titanate (99%; Shanghai Chemi-

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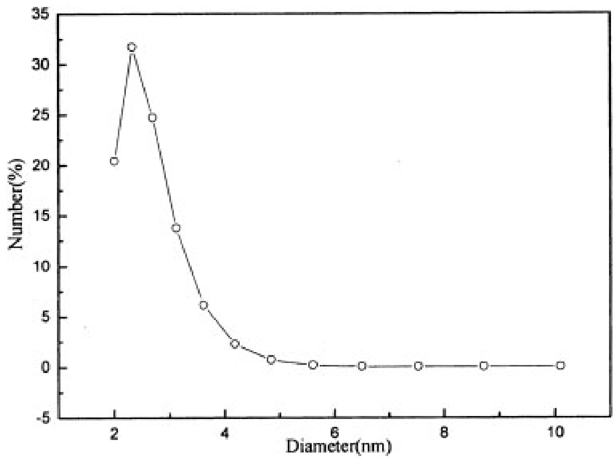

Figure 1 Size dispersion of titanium hydrosol.

cal Reagent), hydrochloric acid (37%), and acetic acid (99.5%; Shanghai Jin Du Reagent Plant).

Preparation of the titanium nanosol

Tetrabutyl titanate was used as the precursor; acetic acid was used to retard the hydrolysis and condensation of tetrabutyl titanate; and hydrochloric acid was used as the catalyst for the hydrolysis. Tetrabutyl titanate was dissolved in the acetic acid at a certain molar ratio, and the solution was agitated until the homogenization was reached. The solution was then slowly added to the hydrochloric acidified water and stirred strongly for 3 h in a three-necked bottle at the ambient temperature. Titanium hydrosol of 2.0% concentration was thus obtained.

Sol–gel treatment

The cotton fabric samples were dip-and-nipped twice in the hydrosol with a pick up of 60–70%. The treated samples were dried at 75°C for 4–5 min and then rinsed with distilled water for 30 s to remove excessive hydrochloric acid and with acetic acid to avoid the damage of fabric when cured at higher temperature. Subsequently, the treated samples were dried and cured at 150°C for 4 min.

Characterization

The size of nanosol was measured by Nanosizer from Malvern Instruments Ltd, UK. The morphological structure of cotton surface was measured by JSM-5600LV of Japan scaning electron microscope (SEM), operating at 10 kV, and the topography of cotton fiber surface was investigated using a NanoScope IV atomic force microscope (AFM; Digital Instruments, USA).

Testing methods

The antibacterial properties of the treated fabrics were quantitatively evaluated with *Staphylococcus aureus* (ATCC 6538) and *Escherichia coli* (ATCC 2666) according to the AATCC Test Method 100. The ultraviolet protection factor (UPF) was measured using UV1000F ultraviolet transmission analyzer made in USA according to AS/NZS 4399–96 standard. The tensile strength was measured according to the ASTM D 5034–95 standard. The tear strength was measured conforming to the Elmendorf method (ASTM D1424–96). The treated cotton samples were washed in the automatic washer according to the AATCC Test Method 135-2000. The handle of samples was tested according to the ASTM D 1388.

RESULTS AND DISCUSSION

Size analysis of sol

The titanium hydrosol was prepared using tetrabutyl titanate as the precursor with hydrochloric acid, acetic

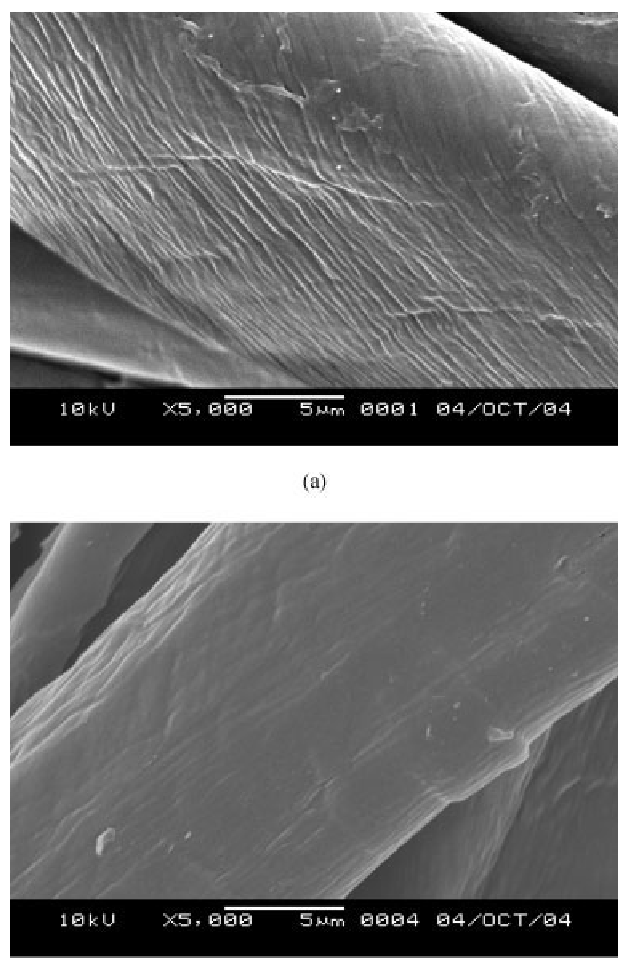

Figure 2 SEM images of cotton fiber. (a) Untreated; (b) Treated with nanosol.

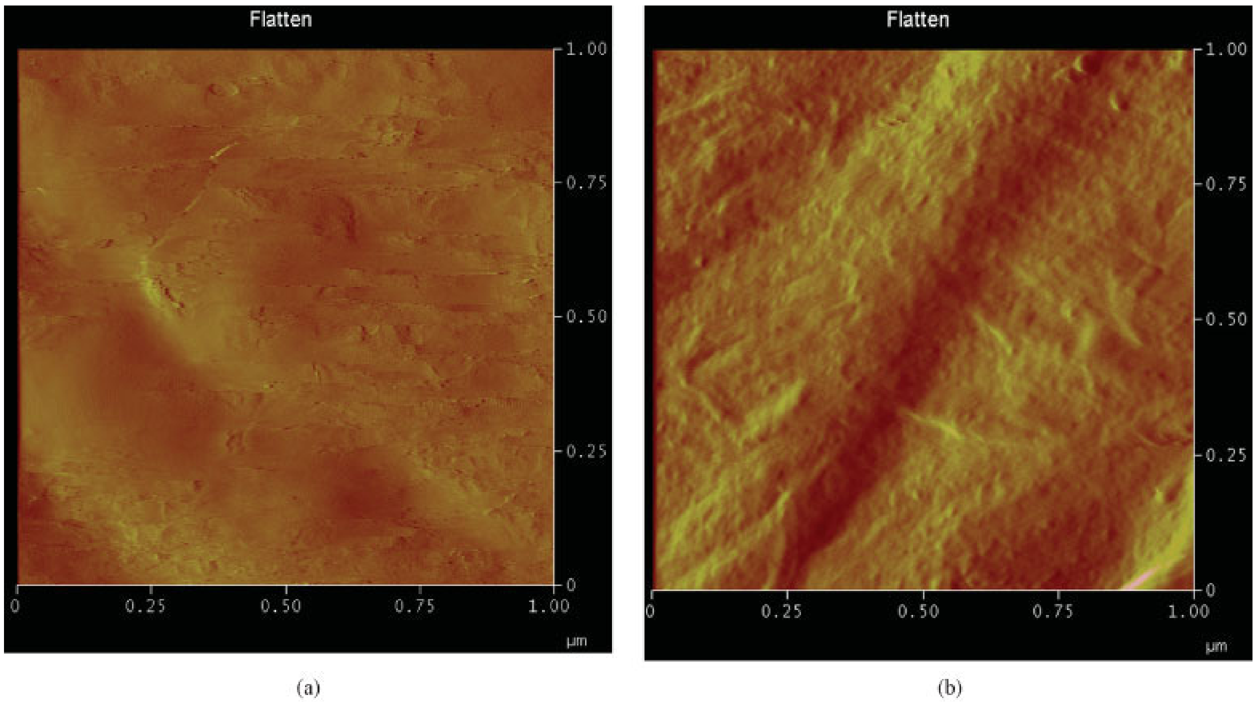

Figure 3 AFM images of cotton fiber. (a) Untreated; (b) Treated with nanosol. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

acid, and water. The present process for the preparation of titanium hydrosol is the reaction of tetrabutyl titanate [Ti $(OC_4H_9)_4$] with water. The dimension dispersion of the formed titanium hydrosol by Nanosizer is shown in Figure 1, where the *x*-axis is the tested diameter of hydrosol (nm), and the *y*-axis is the corresponding number percentage (%).

From the Figure 1, it can be seen that the titanium sol particles are very small after hydrolysis. The size of tested sols was all not more than 10.1 nm, and 99.96% of the sols were less than 6.5 nm, that is, the accumulative number ratio of sol particles smaller than 6 nm almost reaches 100% for the whole sol solution. It indicated the hydrolysis is thoroughly complete and uniform, which was helpful to form rather evener and thinner layer on the fiber to avoid negative effects on the handle and strength.

Morphology analysis of cotton fiber by SEM and AFM

The morphology of cotton fabric surface when treated with the titanium hydrosol is shown in Figure 2.

The grooves and fibrils of untreated cotton fiber [Fig. 2(a)] can be observed clearly, whereas the surface of the treated cotton fiber is covered with a layer of continuous thin film, which looks very smooth through the SEM picture [Fig. 2(b)]. This result is different from that obtained when the absolute ethanol was used as the medium.[10]

To further probe the titanium thin layer, the AFM was applied to characterize the cotton fiber surface shown in the Figure 3.

From the Figure 3, it can be seen that there exist a few bigger gel particles on the surface of the treated cotton fiber [Fig. 3(b)] compared with untreated cotton fiber [Fig. 3(a)], and their dimensions are all less than 50 nm. And obviously, there is a layer of nanoparticles with the size far less than 50 nm [Fig. 3(b)]. Therefore, we can draw a conclusion from the Figures 2 and 3 that the gel particles on the cotton fiber surface are all nanoscaled and tightly link together with interconnected Ti—O—Ti bonds to form an inorganic network.

Antibacterial effects

The antibacterial properties of the treated fabrics were quantitatively evaluated with *S. aureus* and *E. coli*

TABLE I
Antibacterial Property of Cotton Fabrics Treated with Titanium Hydrosol

	Bacterial reduction rate (%)	
	Escherichia coli	*Staphylococcus aureus*
Treated with hydrosol	97.2	96.6
After 50 washing cycles	96.4	95.2

TABLE II
UPF Classification System

UPF range	UV radiation protection category	Effective UV radiation transmission (%)	UPF ratings
15–24	Good protection	6.7–4.2	15,20
25–30	Very good protection	4.1–2.6	25,30,35
40–50, >50	Excellent protection	≤2.5	40, 45, 50, >50

according to the AATCC Test Method 100. Circular fabric swathes (about 1 g) were inoculated with 1.0 ± 0.1 mL of inoculum in a 250-mL jar. The inoculum was a nutrient broth culture containing over 1.0×10^4–10^6 colony-forming units of bacteria per milliliter. After the swathes were inoculated with the bacterium for a contact time of 18 h, the 100 mL of sterilized distilled water was poured into container, which was then vigorously shaken, and the supernatant was subsequently diluted to 10^1, 10^2, 10^3, and 10^4. The dilute-solution aliquots were plated on a nutrient agar that was incubated for 18 h at 37°C, and the viable colonies of bacteria on the agar plate were counted. The bacterial reduction caused by the antibacterial function from the treated fabrics was calculated using the following equation:

$$\text{Reduction rate}(\%) = (A - B)/A \times 100$$

where A is the numbers of bacterial colonies from untreated fabrics, and B is the numbers of bacterial colonies from the treated fabrics.

In our research, the antibacterial property of the cotton fabric by the titanium hydrosol treated is listed in the Table I.

It is well established that the titanium dioxide is the best candidate for photocatalytic applications.[11,12] Under the UV-irradiation of photon energy greater than or equals to the TiO_2 band gap energy ($h\nu > 3.2$ eV, i.e., $\lambda < 380$ nm), the electron-hole pairs are formed, which once dissociated, generate free photoelectrons and holes able to interact with organic matter present at a TiO_2 particle surface. Thus, through a complex multistep heterogeneous photocatalytic process, an oxidative decomposition of organic molecules can be induced so that the bacteria are killed. In addition, Ti element also plays an effect on the inhibition of the metabolism of microorganisms, i.e., stopping its growth.

From the Table I, it can be seen that after the sol–gel treatment, the antibacterial reduction rate with *S. aureus* and *E. coli* of treated fabrics reached 97.2% and 96.4%, respectively, and after 50 washing cycles, the antibacterial properties changed little because of the strong affinity between gel particles and cellulose, and bacterial reduction rate was still kept as high as above 95%.

UV-cutting effects

The Australian/New Zealand standard indicates a system of classification of protective fabrics.[13] For the purposes of labeling, the UV protective clothes should be categorized according to their rated UPF, shown in Table II.

The four cotton fabrics, including the original cotton fabric, the titanium hydrosol-treated cotton fabric, and the treated fabric after 25 and 50 washing cycles, are tested based on the aforementioned method, and the result is shown in Table III and Figure 4.

From Figure 4 and Table III, it can be seen that after the sol–gel treatment the UV transmittance value of the cotton sample decreases obviously, especially in UVB range, because the formed nanoscaled titanium gel particles strongly absorb and reflect the ultraviolet rays, and the UPF value increases from 7.8 to 91.17 accordingly, which reaches the highest level (50) of

TABLE III
Parameters Related to the UPF of Cotton Samples

Samples	Mean UPF	UVA_{AV} (%)	UVB_{AV} (%)	UPF ratings
Untreated	7.8	18.76	10.14	5
Treated with hydrosol	91.17	8.35	0.40	50
After 25washing cycles	90.84	8.69	0.37	50
After 50 washing cycles	86.98	8.90	0.39	50

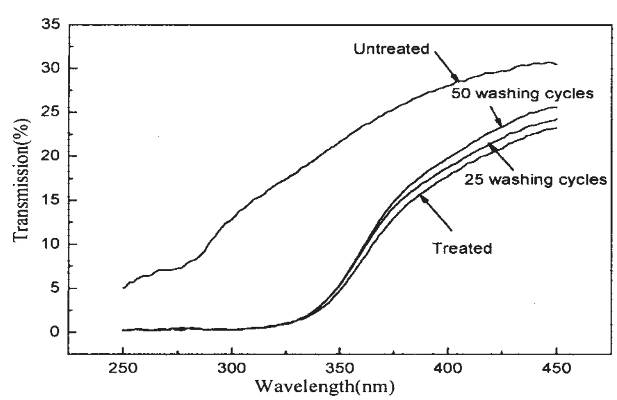

Figure 4 The ultraviolet transmission curves of cotton samples.

TABLE IV
Tensile Strength and Tear Strength of Cotton Fabric Treated with the Sol

	Tensile strength				Tear strength	
	Warp		Weft		Warp	Weft
Samples	Strength (N)	Elongation (%)	Strength (N)	Elongation (%)	Strength (gf)	Strength (gf)
Untreated	661.5	8.65	292.4	14.78	557.2	435.3
Treated	650.3	8.32	288.6	14.41	551.5	430.1
Difference	−1.6%		−1.3%		−1.0%	−1.2%

AS/NZS 4399–96 standard. It should be noted that in the UVA range the absorption of the sample treated with hydrosol is relatively weak. Figure 4 and Table III also show that the UV transmittance after washing is very good, and especially in the range of UVB, the UV transmittance conversely decreased a little, and the UV transmittance in UVA range increased a bit little after washings. Generally speaking, after washings, the UPF changed a little and still kept the highest UPF level probably because of the formation of covalent bonding between the cellulose hydroxyl groups and the hydroxyl groups of titanium hydrogel.

Mechanical properties

For the fabric application, the mechanical properties is the basic requirement. Therefore, the titanium hydrosol-treated fabrics are also tested on the tensile and tear strength, and the results are shown in the Table IV.

From the Table IV, it can be seen that the tensile strength and tear strength of the treated fabric changed a little, which shows that the sol–gel treatment has not played a negative role on the cotton fabric.

When used as the clothing, the handle is very important estimate aspect to its property, where the bending length is measured (Table V).

The handle of the sample treated with the sol was tested in terms of bending length according to the ASTM D 1388, and the results are displayed in Table V. It is clear that the handle of fabrics does not deteriorate after the sol–gel process and as soft as the untreated one.

CONCLUSIONS

When the titanium hydrosol, different from the alcosol, was taken as the treatment method of the fabric, it can display various good functions on the fabric.

TABLE V
The Handle of Samples Treated with the Sol

	Bending length (cm)	
Sample	Warp	Weft
Untreated	5.03	4.21
Treated	5.14	4.30

In this study, the antibacterial and UV-resistant properties of cotton fabrics treated with titanium hydrosol were improved considerably, and after 50 washing cycles, the effect changed little because of the strong affinity between the gel particles and cellulose. The nanogel particles on the fabric were linked together to form inorganic network on the fiber, which can strongly absorb the ultraviolet rays so that the antibacterial and UV-resistant properties both were remarkably enhanced.

At the same time, the strength tests of the treated fabrics showed no negative effects from the treatment on the fabrics, which revealed that the titanium hydrosol can improve the function of the cotton fabric based on the previous property.

Therefore, the sol–gel method can be applied effectively in the textile functional finishing, and the present titanium hydrosol treatment shows promise in future applications.

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