Cotton Fabric Surface Modification for Improved UV Radiation Protection Using Sol–Gel Process

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ABSTRACT: In this study, lightweight 100% cotton fabric was successfully modified by the sol–gel process to impart high ultraviolet radiation (UVR) scattering property to the fabric surface. Active ingredients were tetraethyl orthotitanate [$Ti(OCH_2CH_3)_4$] and tetraethyl orthosilicate [$Si(OCH_2CH_3)_4$]. The cotton fabric was padded with the nanosol solution, dried at 60°C, and cured at 150°C. Scanning electron microscopy showed continuous and uniform film on the fiber surface. Excellent UVR scattering was obtained with all treated fabrics. Increasing titania content in the nanosol solution leads to increased UVR protection. This is attributed to the increase of the refractive index of the film formed on the fabric surface. Excellent durability of the treatment was obtained, which indicates a good adhesion between the coating and the fabric surface. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 111–117, 2007

Key words: thin film; functionalization of polymer; cotton fibers; gel; modification; coatings; ultraviolet radiation

INTRODUCTION

The ultraviolet radiation (UVR) is composed of three types: UV-A (315–400 nm), UV-B (290–315 nm), and UV-C (100–290 nm). The UV-C radiation is absorbed by the ozone layer, however, the UV-A and UV-B reach the earth surface and cause serious health problems such as skin cancer, sunburn, and photo-aging.[1–6] Therefore, special attention has been focused recently on the ultraviolet transmission of textiles because of the growing demand in the marketplace for lightweight apparel that offers protection from UVR, while fostering comfort. Modifying fabrics to reduce the UVR transmission to the wearer is a relatively new application. To quantify the protection from the UVR, the term sun protection factor (SPF) is widely used for cosmetic sunscreens.[2,7] However, for fabrics, the use of the term ultraviolet protection factor (UPF) is preferred.[7] This factor is based on an *in vitro* measurement and is defined as the ratio of the average effective UVR calculated for an unprotected skin to the average UVR irradiance calculated for a skin protected by the fabric.[7] Effective UVR irradiance is defined as the product of the relative erythemal spectral effectiveness by the relative energy value of the solar spectral irradiance reaching the skin.[7]

Several factors affect the ability of fabrics to provide adequate protection from the UVR. Srinivasan and Gatewood conducted an extensive study on the relationship between dye characteristics and the UV protection provided by the cotton fabric.[4] Their results showed that color is not a reliable indicator of the UV protection provided by dyed fabrics. They reported that direct dye black 38 does not necessarily provide the best protection. However, other dyes (such as direct dye red 24, direct dye red 28, direct dye red 80, direct dye blue 1, direct dye blue 86, direct dye blue 218, direct dye green 26, and direct dye brown 154) may increase the UV protection depending on their absorption characteristics in the UV region. Zhou and Crews showed that optical brightening agents used in laundering detergents improved the UV radiation blocking ability of cotton fabrics and cotton/polyester blends.[6] Crews et al. and Algba et al. conducted studies to investigate the factors affecting the UV radiation transmission of undyed fabrics.[3,8] It was concluded that the fabric porosity was the single best predictor of UV-blocking properties of an undyed woven fabrics. Other studies focused on the improvement of the UV protection of fabrics by applying available commercial UV absorbers (such as Cibatex UPF™ for cotton and cotton blend fibers, Cibafast W™ for wool, silk, and polyamide fibers and their blends, and Cibatex APS™ for polyester and its blends).[1,2]

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Recent research has focused on modifying the cotton fabric surface using sol–gel method.[9] Titania hydrosol prepared from tetrabutyl titanate [$Ti(OCH_2CH_2CH_2CH_3)_4$] and fluorescent whitening agents were applied using the sol–gel method to improve UPF of cotton fabric, and to improve the durability of the UVR protection provided by the fabric during the laundering process, a polyacylate binder was used.[9] In another study, titania nanosol was synthesized from titanium tetraisopropoxide as precursor [$Ti(OCH(CH_3)_2)_4$] and applied to the cotton fabric.[7]

In previous research, we reported on a new approach to antibacterial treatment of cotton fabric with dodecanethiol-capped silver nanoparticles using the sol–gel process.[10] In this article, we present the results obtained by treating the lightweight cotton fabric using tetraethyl orthosilicate [$Si(OCH_2CH_3)_4$] and tetraethyl orthotitanate [$Ti(OCH_2CH_3)_4$]. The effects of the precursor concentration and the durability of the treatment to repeated home laundering are presented.

MATERIALS AND METHODS

Materials

The 100% cotton fabric used in this study was desized, scoured, and bleached. The fabric characteristics were: 79.4 ends, 65.4 picks, yarn count of 23.4 × 22 tex, and a weight of 161.98 g m^{-2} (4.8 oz yd^{-2}). The chemicals used to prepare the sol, tetraethyl orthotitanate [$Ti(OCH_2CH_3)_4$], tetraethyl orthosilicate [$Si(OCH_2CH_3)_4$], ethanol (C_2H_5OH), acetic acid (CH_3COOH), hydrochloric acid (HCl) (37.7%) were purchased from Fisher Scientific (Houston, TX). All chemical reagents were used as received.

Titania nanosol preparation

Varying amounts of the precursor $Ti(OCH_2CH_3)_4$ (1, 2, 4, and 6 mL) were first mixed with acetic acid (10 drops) to prevent precipitation of TiO_2 particles upon addition of ethanol and stirred for 2 min. A volume of 56 mL of absolute ethanol was added drop-wise while stirring. Upon completion of ethanol addition, the solution was stirred for 10 min. The sol obtained was clear and homogenous (pH = 1–2).

Titania–silica nanosol preparation

Silica nanosol was first prepared by mixing the precursor $Si(OCH_2CH_3)_4$ (20 mL) with ethanol (10 mL) and stirred for 15 min. Freshly prepared titania nanosol (2, 4, 6, 10, and 15 mL) in 28 mL ethanol was added drop-wise to the silica sol and stirred for 10 min. A solution of ethanol (10 mL) and water (1.5 mL) was added drop-wise. The pH of the resulting solution was adjusted to 1–2 using hydrochloric acid, and the solution was stirred for 45 min.

Fabric treatment

Cotton fabric samples were dipped into the titania nanosol, soaked for 5 min, and passed through a two-roller laboratory padder (BTM 6-20-190) at a speed of 4 yd min^{-1} and an air pressure of 2.76×10^5 Pa. The padded fabric samples were then dried at 60°C for 10 min by passing through a Ben Dry-Cure Thermosol Oven (IT500 with 18-in. working width) at 0.3 yd min^{-1} to evaporate the solvent (ethanol) and then cured in the same oven at 150°C for 5 min at a speed of 0.7 yd min^{-1}. The same process was performed to treat the fabric with titania–silica nanosol mixture. The samples were rinsed under running reverse osmosis water for 5 min, dried and then conditioned at (21 ± 1)°C and (65 ± 2)% relative humidity for at least 24 h before performing analysis. Three replications were performed from each concentration of the precursor.

Scanning electron microscopy

Morphological changes as a result of sol–gel treatment of cotton fabric were investigated using scanning electron microscopy (SEM). Fabric samples were mounted on an aluminum stub and coated with a layer of gold by means of thermal evaporation in a vacuum-coating unit. They were then examined in the scanning electron microscope (Hitachi S570) with an accelerating voltage of 6 keV.

X-rays elemental analysis

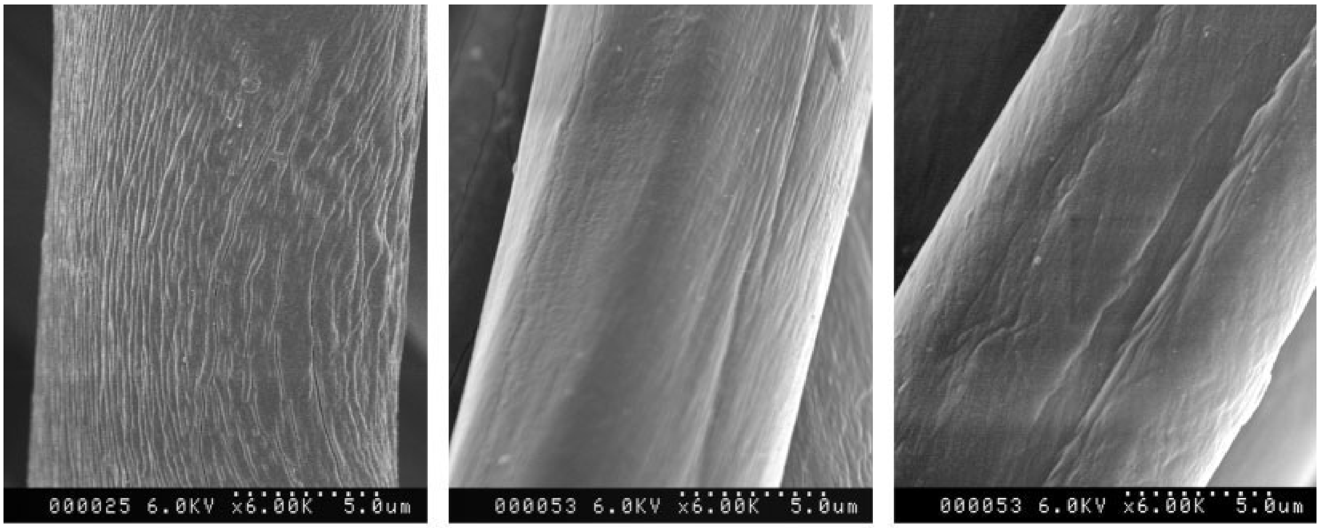
JEM-100CX analytical microscope equipped with KEVEX 8000 X-ray analyzer was operated at 40 keV in SEM mode for imaging and EDAX mode for analysis of characteristic X-ray spectra.

FTIR measurements

Spectrum-One (from Perkin–Elmer) equipped with a universal attenuated total reflectance Fourier transform infrared (UATR-FTIR) was utilized to acquire the FTIR spectra of the treated fabrics. The IR spectra were collected using 32 scans with 4 cm^{-1} spectral resolution between 650 and 4000 cm^{-1}.

Tests of durability of the treatment to repeated laundering

The treated fabric samples were subjected to home laundering up to 40 cycles according to the AATCC standard test method 124-96.[11] AATCC standard de-



(a) (b) (c)

Figure 1 Scanning electron microscopy micrograph of (a) untreated cotton fabric, (b) cotton fabric treated with titania nanosol, and (c) cotton fabric treated with titania–silica nanosols.

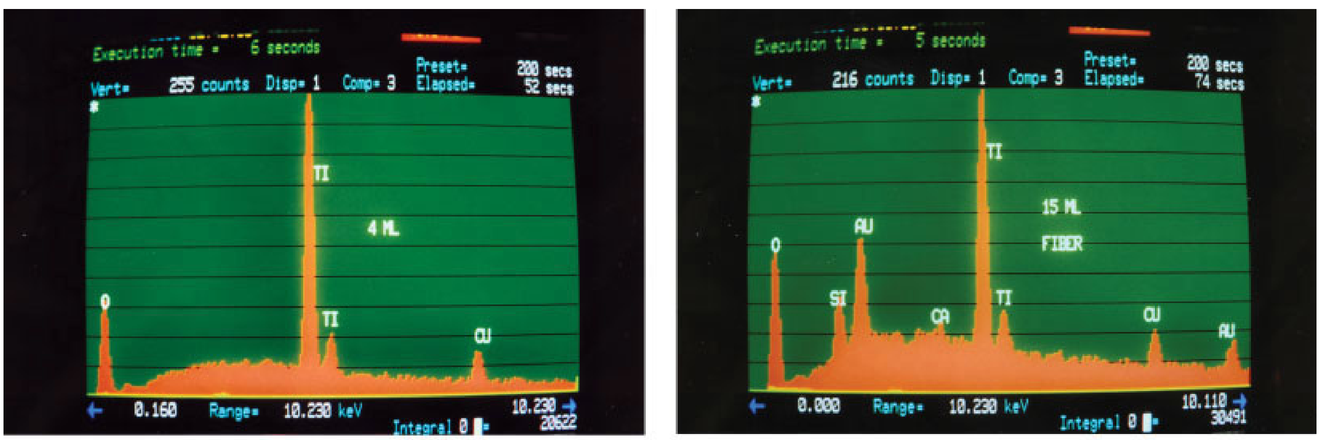
tergent without optical brighteners was used throughout the laundering cycles.

Ultraviolet protection measurement

The UPF was measured using the SPF-290 analyzer (Optometrics, MA). This instrument is equipped with an automated X–Y stage allowing automated measurement. Three specimens (10 cm × 10 cm each) were scanned from each sample and 12 scans per specimen were performed. The UPF (average of 12 scans) was computed using the formula: UPF $= \sum_{290}^{400} E_\lambda S_\lambda \Delta\lambda / \sum_{290}^{400} E_\lambda S_\lambda T_\lambda \Delta\lambda$.[12] In this equation, E_λ corresponds to the relative erythemal effectiveness, S_λ is the solar spectral irradiance, T_λ is the average spectral transmittance, and $\Delta\lambda$ is the measured wavelength interval in nanometers (290 nm ≤ λ ≤ 400 nm).

RESULTS AND DISCUSSION

Figure 1 shows the morphological changes induced by the treatment with titania and titania–silica nanosols. In contrast to the micrograph of untreated cotton [Fig. 1(a)], the micrographs of the treated cotton with titania nanosol or titania–silica nanosol show the formation of smooth and uniform layer on the fiber surface [Figs. 1(b) and 1(c)]. The elemental compositions of the film coating are shown in Figure 2. For the fabric treated with titania nanosol, titanium and oxygen



(a) (b)

Figure 2 X-ray microanalysis of the fabric treated with (a) titania nanosol and (b) titania–silica nanosol. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

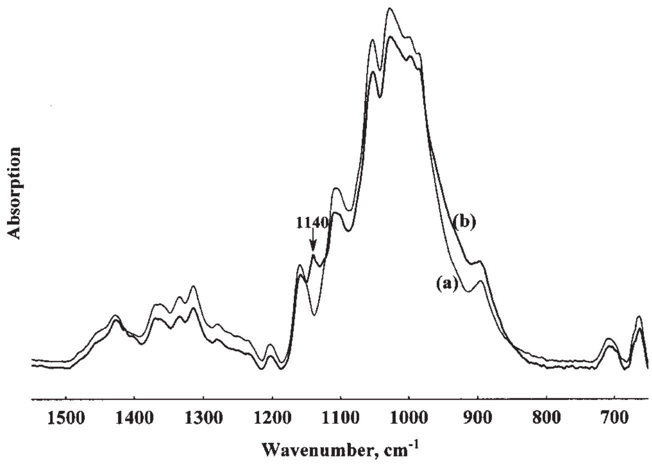


Figure 3 UATR-FTIR spectra of (a) untreated cotton fabric and (b) treated cotton fabric with titania nanosol.

are the only two detected elements in addition to gold and copper due to the gold coating and sample holder [Fig. 2(a)]. For the fabric treated with titania–silica nanosol, silica element is detected in addition to titanium and oxygen elements [Fig. 2(b)]. A small amount of calcium element is also detected as impurity.

Figure 3 shows the FTIR spectra of untreated cotton fabric and treated cotton fabric with titania–silica nanosol. The presence of additional peak at 1140 cm^{-1} could be attributed to the asymmetric stretching of ≡Si—O—Si≡.[13]

Analysis of variance shows a significant effect of the amount of the tetraethyl orthotitanate in the solution on the fabric percent add-on after rinsing and drying (Table I). The increase in add-on results in a significant increase in the ultraviolet protection of the fabric. There is 300% increase in the UPF of the fabric after treatment with a solution containing 1 mL of tetraethyl orthotitanate (Table II). After treatment with a solution containing 4 mL of tetraethyl orthotitanate, the UPF increases by 760% and the fabric provides excellent protection from the UV radiation (UPF ratings 50+). In this case, the amount of the UV radiations passing through the fabric is reduced to less than 1.6%. The evolution of the UPF as function of the amount of the $Ti(OCH_2CH_3)_4$ is shown in Figure 4. The relationship between UPF and the amount of tetraethyl orthotitanate is: UPF $= -1.7945([Ti(OCH_2CH_3)_4])^2 + 21.328([Ti(OCH_2CH_3)_4]) + 8.6953$, $R^2 = 0.99$.

Tables III and IV respectively, show the variance analysis of the percent add-on and UPF of the fabric, treated with mixture of $Ti(OCH_2CH_3)_4$ and $Si(OCH_2CH_3)_4$. Significant effects are observed on both the percent add-on and the UPF. There is an increase of the UPF by 123% when the solution contains 4 mL of $Ti(OCH_2CH_3)_4$. The percent add-on is much higher than the fabric treated with titania nanosol only. The relationship between the UPF and the amount of tetraethyl orthotitanate is: UPF $= 1.6252 ([Ti(OCH_2CH_3)_4]) + 8.2026$, $R^2 = 0.98$ (Fig. 5).

When the fabric is treated with titania nanosol, TiO_2 particles are formed by polycondensation reac-

TABLE I
Variance Analysis: Effect of $Ti(OCH_2CH_3)_4$ Content on the Percent Add-On on the Treated Fabric with Titania Nanosol after Rinsing and Drying

Parameter	df	F	Probability	% Add-on[a]
Intercept	1	3446.82	0.0000001	
$[Ti(OC_2H_5)_4]$	4	650.65	0.0000001	
0 mL				0.00 e
1 mL				0.35 d
2 mL				1.64 c
4 mL				2.52 b
6 mL				4.14 a
Error	10			

df, degrees of freedom; F, variance ratio.
[a]Values not followed by the same letter are significantly different with $\alpha = 5\%$ (according to Newman–Keuls tests).

TABLE II
Variance Analysis: Effect of $Ti(OCH_2CH_3)_4$ Content on the Ultraviolet Protection Factor (UPF) of Treated Fabric with Titania Nanosol

Parameter	df	F	Probability	UPF[a]
Intercept	1	3525.49	0.0000001	
$[Ti(OC_2H_5)_4]$	4	255.07	0.0000001	
0 mL				7.2 e
1 mL				29.0 d
2 mL				47.3 c
4 mL				62.0 b
6 mL				73.3 a
Error	10			

df, degrees of freedom; F, variance ratio.
[a]Values not followed by the same letter are significantly different with $\alpha = 5\%$ (according to Newman–Keuls tests).

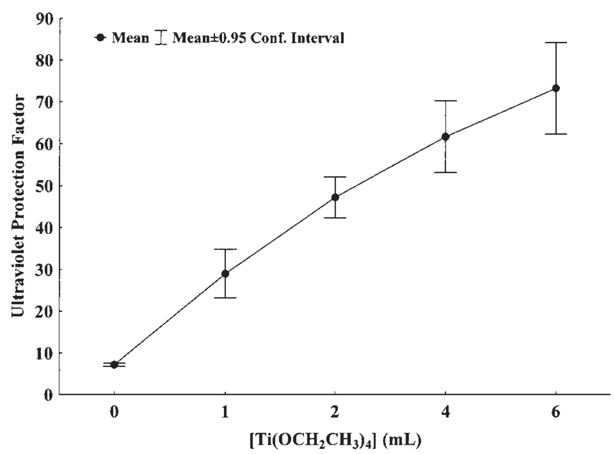


Figure 4 Fabric treated with titania nanosol: UPF versus amount of $Ti(OCH_2CH_3)_4$ in the solution.

TABLE III
Variance Analysis: Effect of $Ti(OCH_2CH_3)_4$ Content in the Titania–Silica Nanosol on the Percent Add-On on the Fabric after Rinsing and Drying

Parameter	df	F	Probability	% Add-on[a]
Intercept	1	64483.89	0.0000001	
$[Ti(OC_2H_5)_4]$	5	2771.82	0.0000001	
0 mL				0.0 e
2 mL				7.1 c
4 mL				5.7 d
6 mL				7.0 c
10 mL				7.6 b
15 mL				8.1 a
Error	12			

df, degrees of freedom; F, variance ratio.
[a] Values not followed by the same letter are significantly different with $\alpha = 5\%$ (according to Newman–Keuls tests).

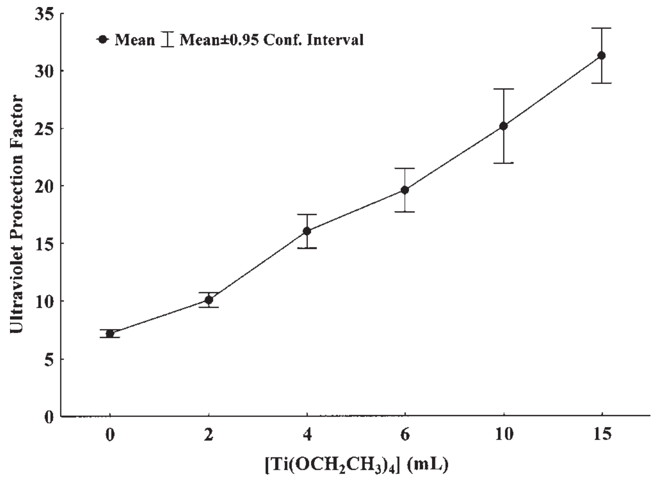


Figure 5 Fabric treated with titania–silica nanosol: UPF versus amount of $Ti(OCH_2CH_3)_4$ in the solution.

tions of $Ti(OCH_2CH_3)_4$. The formation of these particles on the fabric surface imparts very good and efficient UVR scattering because of the large refractive index of TiO_2 particles.[14] This hypothesis is further supported by the increase of the UPF (decrease of the UVR transmission) with increasing amount of tetraethyl orthotitanate in the nanosol formulation. The effects of titania content on the properties of titania–silica films prepared using sol–gel process were investigated.[15] The authors reported that the refractive index of the material is a linear function of the molar concentration of the titania [Refractive index = 1.45 + 0.34(titania content)].

Figure 6 shows the comparison between the monochromatic protection factors of the control fabric, the fabric treated with titania–silica nanosol, and the fabric treated with titania nanosol. This chart shows very good UVR protection especially in the most dangerous range of the UVB (289–315 nm) for the fabric treated with titania nanosol. Better UVB protection is also noticed for the fabric treated with titania–silica nanosol when compared to the control.

To control the effect of the treatment on fabric performance, fabric strength was measured. Table V shows an increase in both load at peak and elongation at peak when the fabric is treated with titania nanosol (10.9 and 48.4%, respectively). However, the treatment with titania–silica nanosol resulted in a decrease in both load at peak and elongation at peak (−39.8% and −43.8%, respectively).

The durability of the treatment to repeated home laundering was evaluated by performing 40 washing–drying cycles according to the standard test method AATCC 124. Figures 7 and 8 show the evolution of the UPF with laundering cycles for fabrics treated with titania nanosol and titania–silica nanosol. There is an unexpected and significant increase of the UPF during laundering cycles for both treatments.

TABLE IV
Variance Analysis: Effect of $Ti(OCH_2CH_3)_4$ Content in the Titania–Silica Nanosol on the Ultraviolet Protection Factor (UPF) of Treated Fabric

Parameter	df	F	Probability	UPF[a]
Intercept	1	9907.13	0.0000001	
$[Ti(OC_2H_5)_4]$	5	410.97	0.0000001	
0 mL				7.19 f
2 mL				10.07 e
4 mL				16.05 d
6 mL				19.61 c
10 mL				25.16 b
15 mL				31.28 a
Error	12			

df, degrees of freedom; F, variance ratio.
[a] Values not followed by the same letter are significantly different with $\alpha = 5\%$ (according to Newman–Keuls tests).

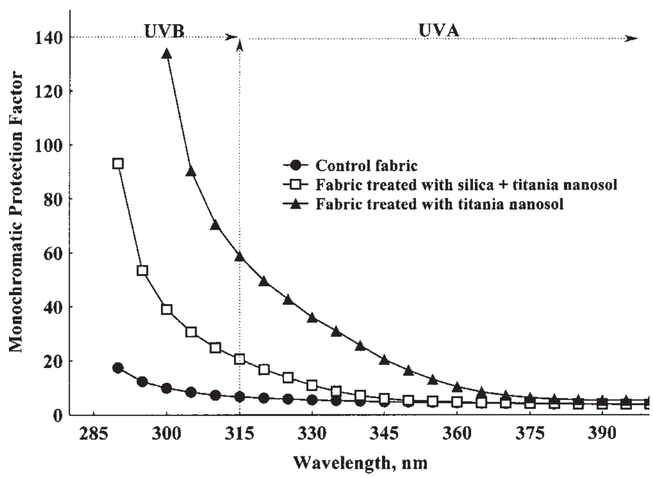


Figure 6 Monochromatic protection factor of control fabric, fabric treated with titania nanosol, and fabric treated with titania–silica nanosol.

TABLE V
Variance Analysis: Effect of the Treatment on the Cotton Breaking Strength and Elongation

Parameter	df	F	Probability	Load at peak (lbf)[a]
Intercept	1	1573.99	0.0000001	
Treatment	2	45.74	0.000002	
Control				76.57 a
Fabric treated with titania nanosol				84.89 a
Fabric treated with silica–titania nanosol				46.09 b
Error	12			
Parameter	df	F	Probability	Elongation at peak (%)[a]
Intercept	1	386.43	0.0000001	
Treatment	2	27.16	0.000035	
Control				6.4 b
Fabric treated with titania nanosol				9.5 a
Fabric treated with silica–titania nanosol				3.6 c
Error	12			

df, degrees of freedom; F, variance ratio.
[a]Values not followed by the same letter are significantly different with $\alpha = 5\%$ (according to Newman–Keuls tests).

(Fabric treated with titania nanosol: df = 12, $F = 50.030$, P-value = 0.000001 ; fabric treated with titania–silica nanosol: df = 13, $F = 132.9$, P-value = 0.000001.) For fabrics treated with titania nanosol, the UPF increased by 270% after 40 laundering cycles. However, for the fabric treated with titania–silica nanosol, the UPF increased only by 65%. The unexpected increase of the UPF during laundering is an interesting phenomenon and further studies are ongoing to elucidate the effect of water during laundering on the structure of film formed on the cotton fabric surface.

The durability and stability of the treatment to multiple home laundering is indicative of a good adhesion between the nanosol film and the fabric surface.[7] The durability of the treatment could be attributed to the formation of covalent linkages between the many hydroxyl groups of cellulose and the hydroxyl groups of the TiO_2 network.[7] It should be pointed out that no binder has been used and no fluorescent agents have been added to the treatment solution.

It has been reported that titania coating exhibits photocatalytic activity.[16] The photocatalytic activity of a material is defined as its ability to create an electron hole as a result of exposure to UVR. The resulting free radicals are very efficient oxidizers of organic matter. Therefore, cotton fabrics treated with titania nanosol may have efficient antibacterial properties and may exhibit self-cleaning and disinfecting properties when exposed to UVR. These treated cotton fabrics could be used successfully in hospital environment. Further experiments are ongoing to quantitatively assess the antibacterial activity of the treated fabric.

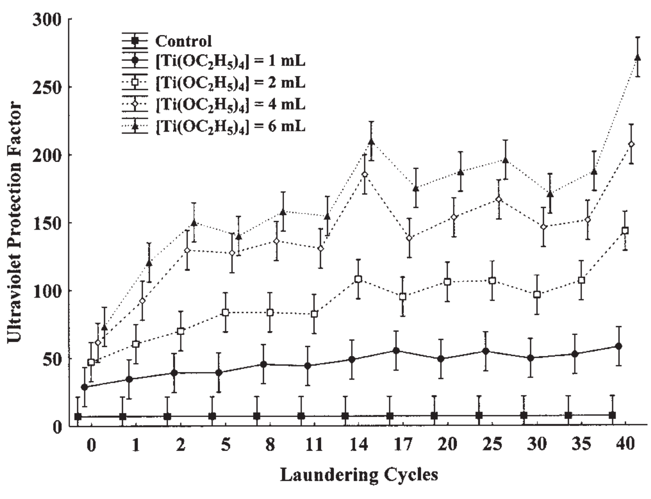


Figure 7 Fabric treated with titania nanosol: UPF versus laundering cycles.

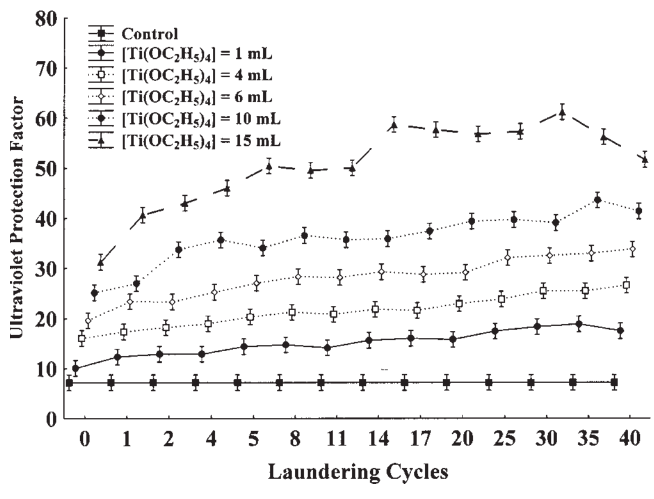


Figure 8 Fabric treated with titania–silica nanosol: UPF versus laundering cycles.

CONCLUSIONS

Lightweight cotton fabric surface was successfully modified with titania and titania–silica nanosol. Titania nanosol was prepared from $Ti(OCH_2CH_3)_4$ and titania–silica nanosol was prepared by mixing $Si(OCH_2CH_3)_4$ and $Ti(OCH_2CH_3)_4$ in the appropriate proportions. Scanning electron microscopy showed the formation of a uniform film on the fiber surface at relatively low treatment temperature (150°C). This treatment imparted excellent UVR protection to the cotton fabric especially in the region of the UVB [290–315 nm]. The formation of covalent linkages between the OH groups of cellulose and the OH groups of titania and titania–silica network imparted excellent durability of the treatment to repeated home laundering. Experiments are planed to test antibacterial properties of the treated fabrics.

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