2210 New approaches for the functionalization of cotton fabrics

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Abstract

In this study, cotton fabric surface was successfully modified by the sol-gel process to impart antibacterial, ultraviolet radiation protection, water repellency, and wrinkle free properties to the fabric. To impart antibacterial property, the cotton fabric was padded with dodecanethiol-capped silver nanoparticles-doped sol, dried at 60ºC, and cured at 150ºC. Scanning electron microscopy showed the presence of a uniform and continuous layer on the fiber surface. The treated cotton fabric showed excellent antibacterial performances against *Escherichia Coli* were examined. To impart ultraviolet radiation protection, cotton fabrics were padded with a titania nanosol solution, dried at 60°C, and cured at 150°C. Excellent ultraviolet radiation scattering was obtained with all treated fabrics. Increasing titanium content in the nanosol led to increased ultraviolet radiation protection. This is attributed to the increase of the refractive index of the film formed on the fabric surface. Excellent durability of the treatment to repeated home laundering was obtained, which could be attributed to the establishment of covalent linkages between the –OH groups of the cellulose and –OH groups of the titania alkoxydes network. Dodecanethiol-capped silver nanoparticles were also incorporated in the titania nanosol. The treated fabric exhibited excellent dual property: antibacterial and anti-ultraviolet radiation. Furthermore, cotton fabrics were successfully functionalized with vinyltrimethoxysilane in order to impart water repellency and good wrinkle recovery.

Keywords: cotton, functionalization, antibacterial, UV protection, wrinkle free

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Introduction

Textile surface modification and functionalization provide a way to impart new and diverse properties to textiles while retaining comfort and mechanical strength. Currently, functional finishes on textile fabrics are of critical importance to improve textile products with multifunctional properties such as antibacterial activity, UV protection, and wrinkle free properties. The sol-gel technology has emerged as a promising way to functionalize fabric surfaces. The sol-gel process has several advantages such as high purity of the deposited film, low temperature processing, ultrahomogeneity, and most importantly the possibility to incorporate additives such as nanoparticles in the first stage of the sol preparation without inhibiting the silica network formation.

To impart antibacterial properties, silver or silver ions were used in previous studies. Silver compounds possess a powerful antibacterial activity, which is generally believed to be caused by the reaction of this heavy metal with proteins (Jeo and Yi, 2003). The chemical reaction of silver atoms with the –SH groups of enzymes inactivates the protein (Jeo and Yi, 2003).

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. Other important functional properties that are of particular interest include water repellency and wrinkle free properties.

In this work, we report on the results of the modification, by the sol-gel process, of 100% cotton fabric to impart antibacterial, anti-UV radiation, wrinkle free, and water repellent properties.

Materials and Methods

The fabric used in this study was desized, scoured, and bleached 100% cotton fabric purchased from Testfabrics (Testfabrics Inc., PA). The characteristics of the fabric were 79.4 ends, 65.4 picks, yarn count of 23.4 x 22 tex, and a weight of 161.98 g/m^2 (4.8 oz/yd^2).

The materials used for antibacterial treatment were: tetraethylorthosilicate $Si(OC_2H_5)_4$, ethanol, 1 N nitric acid solution, deionized water, and silver nanoparticles capped with dodecanethiol (which were prepared as described in previous research) (Korgel, 1999 ; Korgel et al., 1998 ; Brust et al., 1994 ; Korgel et al., 1998 ; Dai et al, 2005).

The chemicals used to prepare the titania nanosol for anti-UV radiation treatment were: tetraethyl orthotitanate ($Ti(OC_2H_5)_4$), ethanol (C_2H_5OH), acetic acid (CH_3COOH), and hydrochloric acid (HCl) (37.7%). Varying amounts of the precursor $Ti(OCH_2CH_3)_4$ (1, 2, 4, and 6 mL) was 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).

The chemicals used to impart water repelleny and wrinkle free properties to cotton fabrics were: Vinyltrimethoxysilane 97% ($CH_2=CH-Si(OCH_3)_3$), water, and HCl. Cotton fabric surface functionalization was carried out in an aqueous environment. Varying amounts of the precursor $H_2C=CH-Si(OCH_3)_3$ (from 0.197 to 4.913 $mol.l^{-1}$) was added drop-wise to distilled water containing four drops of concentrated hydrochloric acid. The pH of the solution was around 3.5. After complete addition of the $H_2C=CH-Si(OCH_3)_3$, the solution was stirred for 10 min. The solution obtained was clear and homogenous.

Cotton fabric samples were dipped into the solution, 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 $2.76x10^5$ Pa. The padded fabrics were then dried by passing them through a Ben Dry-Cure Thermosol Oven. Drying temperatures were 60^oC for 10 min for fabrics treated with silica and titania nanosols (to evaporate to evaporate ethanol) and 100^oC for 4 min (to evaporate water). Finally, the fabrics were cured in the same oven at 150^oC for 4 min. The samples were rinsed under running Reverse Osmosis water for 5 min, dried and then conditioned at 21 ± 1^oC and 65 ± 2% Relative humidity for at least 24 h before performing fabric testing. Three replications were performed from each concentration of the precursor.

Results and Discussion

Antibacterial property: Antibacterial performances of the treated fabric against *Escherichia coli* were performed by measuring the optical density at 600 nm of the medium containing the bacteria culture and the fabric at different times (Figure 1). There are significant differences in antibacterial effects between the untreated cotton fabric, cotton fabric treated only with the sol, and the cotton fabric treated with the sol doped with dodecanethiol-capped silver nanoparticles-rich organic phase (Tarimala et al, 2006). As expected the untreated fabric did not show any antibacterial activity; there is a 20 times increase in optical density, therefore in bacteria population, in a 215 min period (optical density at t = 0 was 0.07, optical density at t = 215 min was 1.5). However, when the fabric is treated with a sol containing 15 mL of the dodecanethiol-capped silver nanoparticles – rich organic phase, the density of the bacteria has **dropped by 40%** (optical density at t= 0 was 0.1, optical density at t = 185 min was 0.06). This behavior indicates that not only an inhibitory effect of the treated fabric on *Escherichia coli* growth, but also suggests a bactericidal activity of the treated fabric (Figure 2).

UV protection property: When the fabric is treated with titania nanosol, TiO_2 particles are formed by hydrolysis / polycondensation reactions 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 (Abidi et al, 2007). The treatment of the fabric with titania nanosol increased the Ultraviolet Protection Factor (UPF) by 918%. Furthermore, excellent durability to home laundering was obtained (figure 3). Dodecanethiol-capped silver nanoparticles were introduced in the titania nanosols and the fabric was treated with this formulation. Excellent antibacterial activity along with excellent UV radiation protection was obtained (Figure 4).

Water repellent and wrinkle free: When the fabric is treated with CH_2=CH-Si$(OCH_3)_3$, silanol groups (resulting from hydrolysis of Si-O-CH_3 groups) could react with the hydroxyl groups (-OH) of the cellulose macromolecules (b(1-4)D-anhydroglycopyranose), leading to the formation of a cross-linked cellulosic chains (Abidi et al., in press). This cross-linkage replaces hydrogen bonds between cellulose macromolecules by covalent bonds. Therefore, the cellulosic chains slippage that normally occurs in untreated cotton fabric, when subjected to a deformation, is prevented. Consequently, functionalized cotton fabric could have wrinkle resistant properties. The statistical analysis showed significant effect of the increase in CH_2=CH-Si$(OCH_3)_3$ concentration on the wrinkle recovery angle (Table 1). The treatment of the cotton fabric with a solution containing 3.603 $mol.l^{-1}$ of CH_2=CH-Si$(OCH_3)_3$ improved the wrinkle recovery angle by 80%. This means that the tendency of the functionalized cotton fabric to recover from a deformation is higher than for the untreated fabric, thus, producing a wrinkle free fabric. There is a slight decrease of the wrinkle recovery angle when the CH_2=CH-Si$(OCH_3)_3$ concentration is higher than 3.603 $mol.l^{-1}$. A possible explanation of this behavior is that at higher CH_2=CH-Si$(OCH_3)_3$ concentration, the formation of polysilane network (poly-condensation of more than 2 CH_2=CH-Si$(OCH_3)_3$

molecules) results in larger molecules that can not travel between cellulosic chains and establish covalent links with the cellulose. Therefore, cellulose chains slippage could occur.

Polycondensation reactions between Si-OH groups leads to the formation of a polysilane network. Because of its size, this polysilane network, would probably not diffuse between the cellulosic chains and establish crosslinks. It will react preferably with the surface OH groups of the cellulose (Bledzki et al., 1996). This process allows the functionalization of the cotton fabric surface by introducing several vinyl groups ($-CH=CH_2$). To assess the hydrophobicity of the functionalized cotton fabric surface, the water contact angles were measured. The untreated bleached cotton fabric surface was hydrophilic (contact angle = 0). At low concentration (< 1.114 $mol.l^{-1}$), the treated fabric remained hydrophilic (table 2). Then, the increase of the $CH_2=CH-Si(OCH_3)_3$ concentration leads to a significant increase of the contact angle and the cotton fabric surface becomes hydrophobic. This result suggests that when the concentration is above 1.114 $mol.l^{-1}$, the functionalized cotton surface becomes densely populated with ºSi-$CH=CH_2$ chains that isolate the native cellulose surface from being in contact with water or other fluids. There is slight linear increase of the water contact angle between 1.114 $mol.l^{-1}$ and 4.913 $mol.l^{-1}$.

Conclusion

In this study we investigated the functionalization of the cotton fabric surface to impart new properties using the sol-gel process. The sol-gel process has been proven to be a suitable technique to form a thin film on the fiber surface and, therefore, modify the properties of the fabric. We have successfully imparted antibacterial, anti-UV radiation, water repellency, and wrinkle free properties to light weight cotton fabric.

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Table 1. Variance Analysis: Effect of VTMS concentration on the wrinkle recovery angle.

Parameter	df[†]	F[†]	Probability	Wrinkle recovery angle (°) [‡]
Intercept	1	12006.81	0.000001	
[$(CH_3$-$O)_3Si$-$CH=CH_2$] (mol.l^{-1})	9	56.07	0.000001	
0				145.1 e
0.197				150.5 e
0.655				161.0 e
1.114				186.3 d
1.638				204.1 c
2.293				246.0 a
2.948				252.6 a
3.603				260.7 a
4.258				247.8 a
4.913				222.2 b
Error	29			

[†] df, degrees of freedom; F, variance ratio.

[‡] Values not followed by the same letter are significantly different with a = 5% (according to the Newman-Keuls test).

Table 2. Variance Analysis: Effect of VTMS concentration on the water contact angle.

Parameter	df[†]	F[†]	Probability	Water contact angle (°) [‡]
Intercept	1	96845.97	0.000001	
[$(CH_3$-$O)_3Si$-$CH=CH_2$] (mol.l^{-1})	7	4695.74	0.000001	
0.197				0 e
0.655				0 e
1.114				103 d
1.638				104 d
2.293				112 c
3.603				113 c
4.258				118 b
4.913				125 a
Error	136			

[†] df, degrees of freedom; F, variance ratio.

[‡] Values not followed by the same letter are significantly different with a = 5% (according to the Newman-Keuls test).

Figure 1: Antibacterial performance test of the control and treated cotton fabric with a silica sol containing different amounts of dodecanethiol-capped silver nanoparticles.

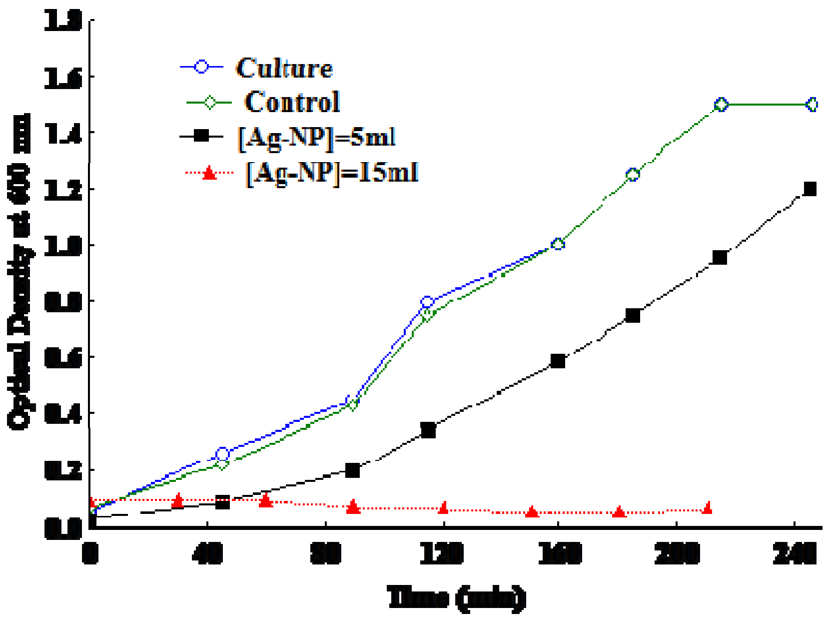

Figure 2: Bactericidal performances of cotton fabric treated with a sol containing dodecanethiol-capped silver nanoparticles-rich organic phase.

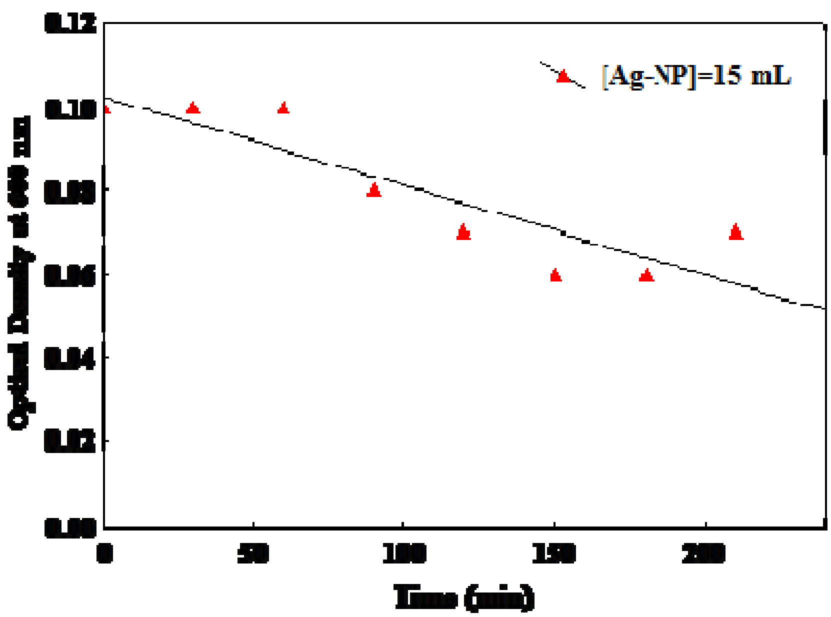

Figure 3: Fabric treated with titania nanosol: UPF versus laundering cycles.

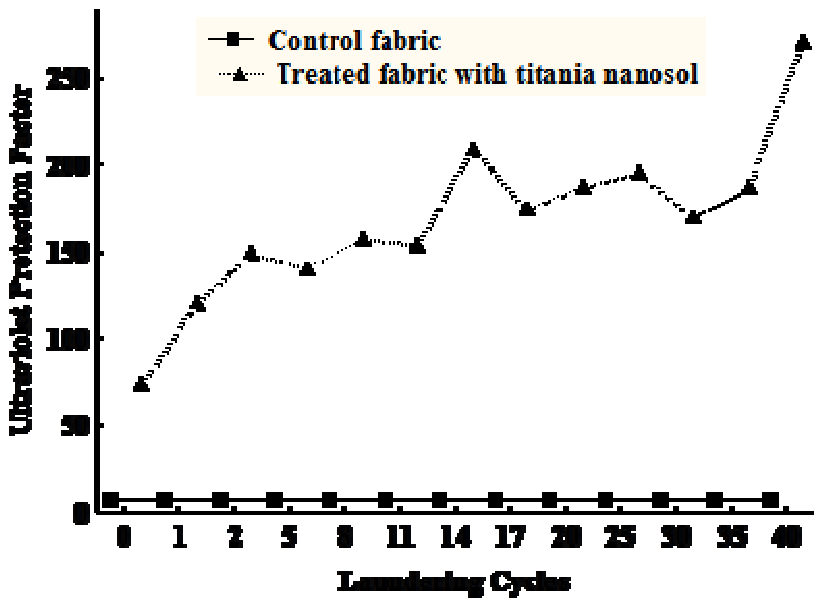

Figure 4: Antibacterial performances of the control and treated cotton fabric with a sol containing titania and Ag-NP.