Antiwrinkle Treatment of Cotton Fabric with a Mixed Sol of TEOS-TTB/DMDHEU

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ABSTRACT: This research explored the effect of a mixed sol on the physical properties of a treated fabric, and confirmed the crosslinkage of SiO_2 and dimethyloldihydroxyethyleneurea (DMDHEU) using Fourier transform infrared (FTIR) spectroscopy and nuclear magnetic resonance (NMR). In the experiment, DMDHEU was applied to a cotton fabric and different mole ratios of tetraethoxysilane (TEOS)/titanium (IV) *n*-butoxide (TTB) were added. The mixture was then subjected to immersion, padding, drying, and curing. The results showed that hydrogen bonds had formed between SiO_2 and DMDHEU. The treated fabric had improved antiwrinkle properties, tensile-strength retention, and yellowing degree when the mole ratio of TEOS was increased. By contrast, the softness of the fabric showed the opposite trend. When the mole ratio of TEOS/TTB was set at 10/1, the treated fabric showed a significant reduction of its antiwrinkle properties under both dry and wet conditions. The fabric treated with TEOS/TTB was superior to the traditionally treated fabric in terms of its ultraviolet (UV) light resistance. When the mole ratio of TEOS/TTB was 2.5/1 or 5.0/1, the addition of 10% DMDHEU during the treatment of the cotton fabric, followed by drying for 5 min at 80°C and curing at 150°C for 2 min, resulted in the fabric having improved and more balanced physical properties. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 2559–2564, 2007

Key words: FTIR; mixing; NMR; strength; stiffness

INTRODUCTION

As the quality of life of individuals increases, so does the demand for improved fabrics. People are concerned not only with the appearance of fabrics, but also with their functionality. Therefore, the question of how to produce multifunctional fabrics has become a major research area over the past few years. Nanograded materials have components that range in size from 1 to 100 nm. These materials are structurally and functionally unique, and have an enormous range of potential applications. Nanofunctional materials and nanotechnology have become priority research topics throughout the world. The integration of nanotechnology and textiles will allow fabrics to become more multifunctional and increase their value, thereby having a huge economic impact. Nanotechnology is currently applied in the development of ultraviolet (UV) light resistance, antistatic properties, infrared (IR) light resistance, antibacterial properties, and water and oil repellence.[1–6] Sol–gel technology, which is used to prepare nanograde inorganic oxide gel solutions, provides a new way to functionalize fabrics by improving their physical properties.

A gel solution (sol) is a medium in which 1–100-nm particles (basic units) are dispersed, whereas the gel itself is a solid reticular substance in which submicroscale holes and polymerizing chains are connected to each other. The sol–gel method allows metallic organic or inorganic substances to undergo gelatification, and to subsequently form oxides or other solid compounds by curing.[7] The sol–gel method has various advantages compared with other techniques.[8–11] First, it can be carried out at low temperatures, making the process easy to control. Second, the purity of the product is high, and the solvent can easily be removed during the handling period. Third, it can make high even material. Fourth, it can be used to produce materials of various shapes. During the finishing process for cotton fabrics, the crosslinking reagent forms links between fiber molecules, which consequently become firm and straight.[12,13] However, the acidic catalyst tends to degrade fibers at high temperatures, leading to a substantial loss of tensile strength.[14–16] Currently, dimethyloldihydroxyethyleneurea (DMDHEU) is most commonly used in the industry, because of its relatively low cost and superior results. However, DMDHEU produces free formaldehyde when it is used in this process. Efforts have therefore been concentrated on the development of a finishing agent that does not produce free formaldehyde. Yet, despite the work of many experts over the past few years, no suitable alternative has been found and the industry still relies on DMDHEU. The sol–gel method utilizes metallic alkoxides as precursors, which can be hydrolyzed under mild conditions and polymerized to a gel solution. The solvent is then

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vaporized or heat treated, and the solution is transformed into an oxide gel with a reticular structure—that is, the gel particles aggregate to form a reticular structure in which the interactive forces include electrostatic forces (such as hydrogen bonds) and Van der Waals forces.[17] When SiO_2 or a nanogel solution of other metallic oxides is used to process fabrics, after drying to eliminate the organic solvent, a layer of oxide-dried gel membrane with a porous structure can form on the fabric surface. Initially, the particles of the original nanogel solution form a three-dimensional reticular structure, which can further increase the tensile strength of the fabric. Then, the titanic anhydride decomposes the free formaldehyde of the fabric, and produces carbon dioxide and water through UV irradiation from sunlight.

As it is relatively easy to change the chemical and physical properties of nanogel solutions, we previously showed that using different types of nanogel solution made it possible to improve the wearing functions of fabrics, and to increase the values of textiles.[18] Few previous research reports have described the application of the sol–gel technique to fabrics. Our previous report was that the better tensile-strength retention (TSR) of treated cotton fabrics was got with DMEU/SiO_2 mix sol.[19] However, based on its fundamental principles, employing this technique to produce functional textile products should be both feasible and worthwhile.

Taking into account the current usage conditions in the industry, and the requirements for multifunctionality and ''green'' environmental concerns, alkoxy silane and titanium (IV) *n*-butoxide (TTB) were hydrolyzed under a catalyst, and a condensation reaction was carried out using the sol–gel technique. The resulting sol was then mixed with DMDHEU to produce a finishing agent for cotton fabrics, which defended them against both wrinkling and UV damage.

EXPERIMENTAL

Materials

Experimental-grade tetraethoxysilane (TEOS) and TTB were purchased from ACROS (USA). Experimental grade sodium lauryl sulfate (SLS), ethyl alcohol, and magnesium chloride were purchased from Wako Pure Chemical Industry (Japan). Industrial-grade DMDHEU (30% solid content) and softening agent (Ailigen) were purchased from the Cyanamide Company (Taiwan) and BASF, respectively.

Method

To produce the sol, an appropriate amount of TEOS was mixed with 15 mL ethanol and 50 mL distilled water in a beaker. The mixture was then stirred for 60 min at room temperature. Next, an appropriate amount of TTB was added, and the resultant mixture was stirred for another 30 min. To produce the sol solution, an appropriate amount of DMDHEU was prepared, and $MgCl_2$ plus 10% DMDHEU was added to 1 g/L softening agent (Ailigen) and 15 mL distilled water; then the mixture was stirred for 30 min. Next, the sol was added to the finishing solution, distilled water was added to reach a volume of 100 mL, and the solution was stirred for 20 min. The cotton fabric was then soaked in the finishing solution using an alternate dipping and padding method (with a pick-up of 85%). Following predrying for 5 min at 80°C, and curing for 2 min at different temperatures (130–160°C), the treated fabrics were washed in a solution containing 1% SDS, rinsed in water, dried, sealed in bags, and placed into a drying machine to prepare them for testing their physical properties.

Analysis and measurement

The Fourier transform infrared/attenuated total reflectance (FTIR/ATR) spectra of the finished fabrics were recorded with a Bio-Rad Digilab FTS-200 spectrometer using an MCT detector. A diamond crystal was used as the internal reflectance element. The single-beam spectra were the result of 64 scans. The spectral resolution was 4 cm^{-1}. The chemical shifts of ^{29}Si and ^{13}C in the treated fabrics were measured with a solid-state nuclear magnetic resonance (NMR) spectrometer. The samples were analyzed using a Bruker Avance 400 ^{13}C-NMR spectrometer at 50 MHz,

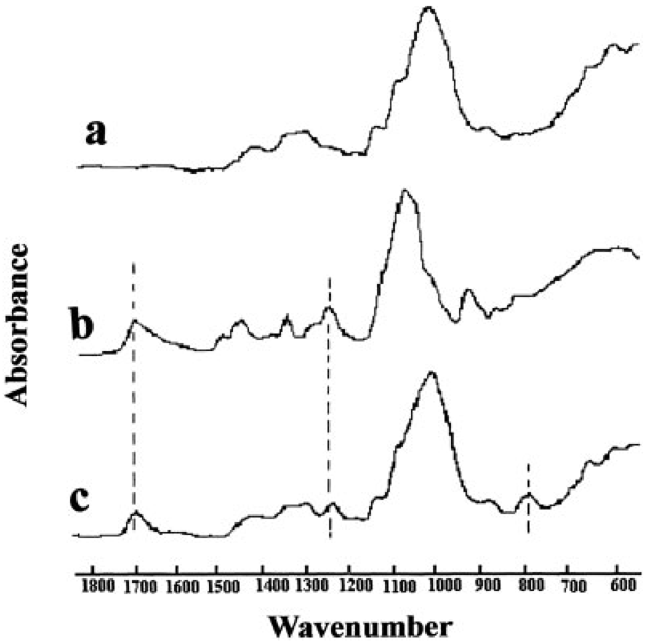

Figure 1 FTIR of treated fabrics. (a) Greige fabric, (b) only with 10%DMDHEU (150°C), and (c) combine TEOS/TTB = 5/1 (150°C).

and the spectra were observed under cross-polarization, magic-angle sample spinning, and power-decoupling conditions with a 90° pulse and a 4-s cycle time. The surface morphologies of the films were observed with a JEOL model JSM 6400 scanning electron microscope. A gold coating was deposited on the samples to avoid charging the surface.

The dry and wet antiwrinkle angles of the treated fabrics were measured according to American Society for Testing and Materials (ASTM) standard D1295-67.[20] The yarn tensile strength was measured by an Alphaten 400 pull tester according to ASTM standard D1682-64. The Mecasys OPTIZEN 2120 UV radiation analyzer was used to determine the anti-UV light resistance of the samples, according to Australia/New Zealand standard (AS/NZS) 4399 : 1996, at a wavelength of 280–400 nm with a penetration rate of 340 nm being used as a benchmark. The evaluation standards are listed in the table below.

UV protection factor (UPF) value	UV protection classification	Transmittance (%)
15, 20	Fair	6.7–4.2
25, 30, 35	Excellent	4.1–2.6
40, 45, 50, 50+	Extremely excellent	<2.5

The softness, whiteness, and yellowness of the treated fabrics were examined by an INTECO softness tester with a 45° tilted platform and a Nippon ND 300A color-difference meter Investigations of the

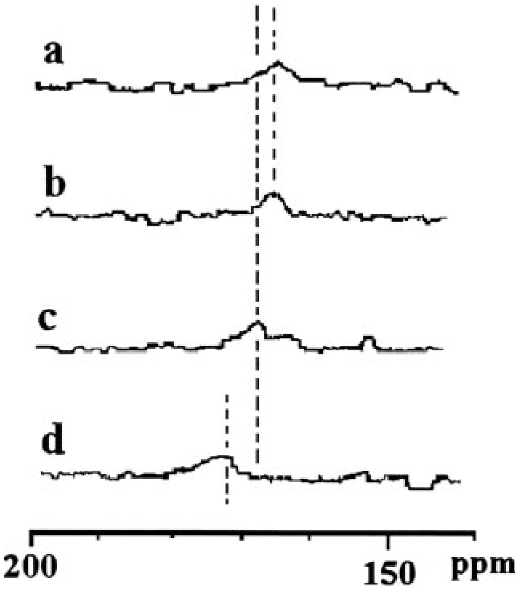

Figure 2 ^{13}C-NMR of fabrics which were treated with different mole ratio of TEOS/TTB. (a) no added TEOS/TTB; (b, c) 5/1; (d) 10/1. (a, c, d) 150°C curing; (b) 130°C curing.

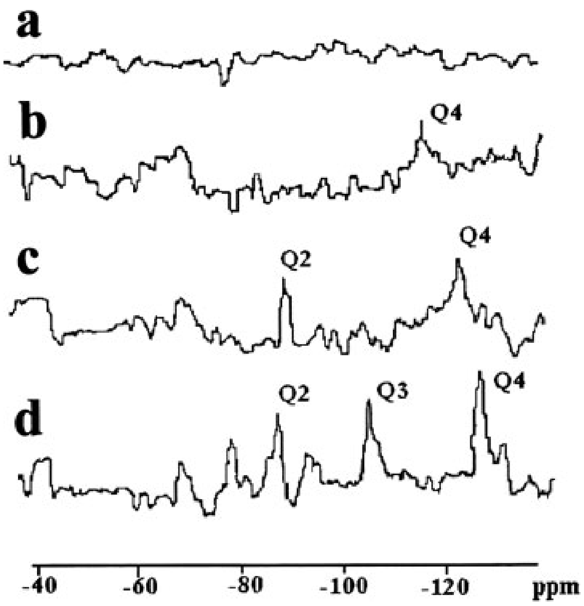

Figure 3 ^{29}Si-NMRof treated fabrics. Symbols same as that in Figure 2.

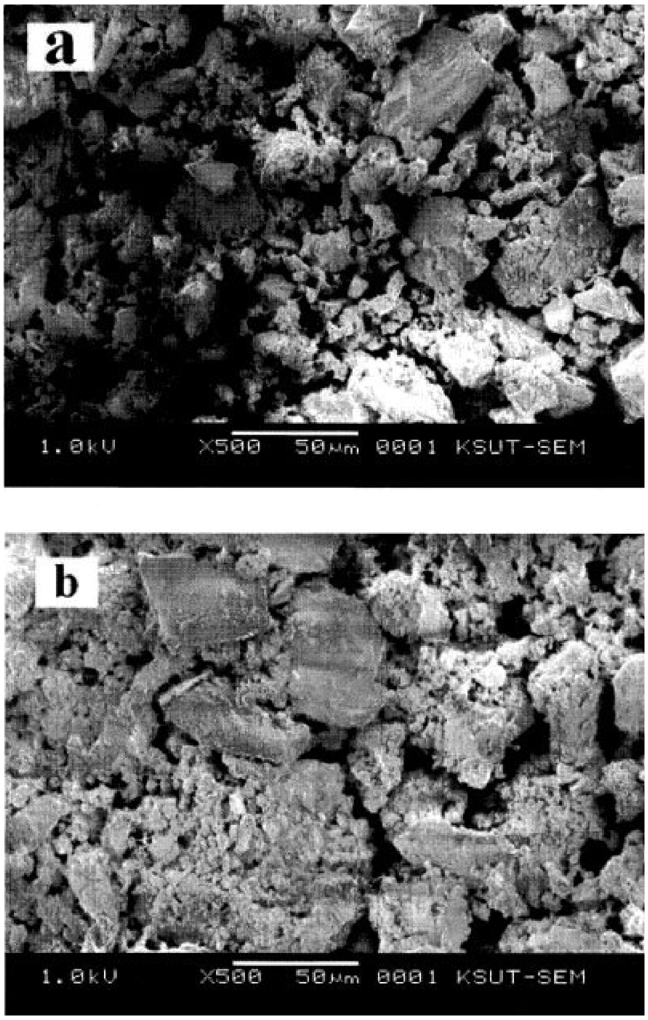

Figure 4 SEM of SiO_2/TiO_2. (a) TEOS/TTB = 5/1 and (b) TEOS/TTB = 10/1.

leaching behavior were performed at 40°C using a Rapid H-type dyeing machine (Taiwan). A 1% aqueous solution of SDS (pH 7) was used as a washing solution. After leaching for 20 min, the textile samples were rinsed intensively with water, dried at room temperature, and their physical properties were reinvestigated after washing 20 times.

RESULTS AND DISCUSSION

FTIR spectroscopy

Figure 1 shows the results of the FTIR analysis of the treated fabric. The results for the untreated fabric are shown in Figure 1(a). The absorption peaks at 1103 and 1159 cm^{-1} corresponded to C—O—C, while those at 1031 and 1053 cm^{-1} corresponded to C—OH. The fabric traditionally treated with DMDHEU is shown in Figure 1(b). One distinct difference was the absorption peak at 1710 cm^{-1}, which corresponded to the C=O in DMDHEU. In addition, an absorption peak of C—N was visible at 1252 cm^{-1}, which confirmed the existence of a crosslink reaction between the cotton fabric and DMDHEU. When TEOS/TTB was involved in the process, a significant change was observed, as illustrated in Figure 1(c). An absorption peak of Si—O—Si in TEOS emerged at 800 cm^{-1}, and the absorption peak shown at 1252 cm^{-1} in Figure 1(b) shifted to 1260 cm^{-1} in Figure 1(c), because the addition of TTB caused a shift in the Ti—O—C group.

NMR analysis

Figure 2 shows the ^{13}C-NMR analysis of the treated fabric. For the fabric treated with DMDHEU in a traditional way, an obvious absorption peak was visible at 166.73 ppm, which corresponded to C=O. When different mole ratios of TEOS/TTB were added and curing was carried out at different temperatures, the ^{13}C chemical position of the treated fabric shifted to a higher-frequency zone as the TEOS mole increased [for example, from 168.18 ppm in Fig. 2(b) to 170.24 ppm in Fig. 2(c), to 171.28 ppm in Fig. 2(d)]. This showed that the more TEOS was hydrolyzed, condensed, and polymerized, the more left-over OH radicals reacted with the C=O radicals of DMDHEU to form hydrogen bonds.

Figure 3 shows the ^{29}Si-NMR analysis of the treated fabric. The higher the proportion of TEOS, the more likely it was for Q3 and Q4 to be hydrolyzed [for example, 109.8 and 125.7 ppm in Fig. 3(d)]. At the same time, the higher temperature of curing, the more likely the polycondensation of Q4 was to occur [for example, 119.6 ppm in Fig. 3(c)]. The fabric treated only with DMDHEU did not contain Si, and so no chemical deviation was shown for ^{29}Si in Figure 3(a). It

TABLE I
Physical Properties of Treated[a] Fabrics

TEOS/TTB mole ratio	Curing temperature (°C)	Properties				
		DCRA (W + F)°	WCRA (W + F)°	TSR (%)	Softness (cm)	Yellowing index
0/0 (no added)	130	257	237	55.5	5.2	3.5
	140	268	246	51.8	5.0	3.8
	150	287	254	47.7	4.8	4.8
	160	290	261	42.3	5.1	5.4
0.75/1	130	274	248	56.4	5.3	4.2
	140	284	257	52.8	5.5	4.8
	150	289	260	48.2	5.8	5.5
	160	297	267	43.9	5.6	6.6
1.5/1	130	278	251	57.1	4.8	4.2
	140	288	261	53.2	5.5	4.4
	150	292	265	49.5	5.4	4.9
	160	297	272	44.8	5.4	5.7
2.5/1	130	281	255	58.5	5.2	3.9
	140	290	263	53.9	5.2	4.0
	150	296	270	50.1	5.3	4.3
	160	301	278	45.1	5.5	5.1
5.0/1	130	284	258	59.2	4.9	3.8
	140	293	265	53.9	5.1	3.8
	150	299	274	51.1	5.2	4.2
	160	304	282	45.7	5.3	4.8
10/1	130	252	241	54.7	5.8	3.3
	140	264	250	50.8	5.6	3.7
	150	270	256	48.2	5.7	3.8
	160	283	260	43.1	5.7	4.6

[a] DMDHEU, 10%; $MgCl_2$, 1%; soft agent, 1%.

TABLE II
Anti-UV Properties of Treated Fabrics

Samples	A	B	C	D	E	F
Transmittance (%)	5.08	4.91	0.23	0.23	0.18	0.78

A: Greige; B: with 10% DMDHEU, 150°C curing; C–F: combined TEOS/TTB = 5/1; C: 130°C; D: 140°C; E: 150°C; F: 160°C.

was clear from the above analysis that the interaction between TEOS/TTB and DMDHEU could affect the crosslinkage of Si with the original fabric, and hence, result in a better reticular structure. As a result, the cotton fabric had higher TSR.

SEM analysis

Figure 4 shows an SEM image of the finishing solution after it had been dried and cured. Figure 4(a,b) illustrates two types of finishing solution with different TEOS/TTB proportions; the larger particles are TiO_2, while the smaller particles are SiO_2. The particles in Figure 4(a) are fine and distinct, whereas those in Figure 4(b) are larger and an agglomeration of SiO_2 is clearly discernable. This was the major cause of the reduced interlinkage reaction between the fabric and the finishing solution.

Influence on the physical properties

Table I shows the measured physical properties of the treated fabrics. The antiwrinkle properties of the treated fabric improved as the curing temperature increased, while the TSR showed the opposite trend. This was mainly because the higher the curing temperature, the more opportunities there were for interlinkage reactions, while at the same time, the fabric underwent oxidation and decomposition to a greater extent. The yellowing was most obvious at a curing temperature of 160°C, while the softness was less easily affected by the curing temperature. The physical properties of the treated fabric were also affected, to a great extent, by the addition of the TEOS/TTB mixed sol to the finishing solution. The dry crease recovery angle (DCRA), wet crease recovery angle (WCRA), and TSR of the treated fabrics were enhanced in proportion to the increase of the TEOS concentration. This was because, when treated, the TEOS/TTB mixed sol combined with the fabric or DMDHEU to form hydrogen bonds, and thus promoted the wrinkle resistance and strength of the treated fabric. However, if the TEOS concentration exceeded a limit, larger particles were formed as a result of an agglomeration forming with other agents. This rendered it difficult for the particles to permeate into the fiber molecules, and for the interlinkage reaction with the fabric to occur. Thus, an excessively high TEOS concentration did not improve the antiwrinkle properties and strength retention. As there was a relatively large amount of SiO_2 on the fabric surface, the yellowing of the treated fabric could be improved.

Table II shows the measured UV light resistance of the treated fabric. According to the AS/NZS 4399 : 1996 assessment standard, if the penetration coefficient is lower than 3.0 or the UPF coefficient is higher than 30, the fabric should be regarded as possessing ideal UV light resistance. So, according to the penetration coefficients shown in Table II, the fabric treated with TEOS/TTB finishing solution showed relatively good UV light resistance, while the original fabric and that treated with DMDHEU in a traditional way showed no UV light resistance. This difference could be explained by the presence or absence of TiO_2 in the treated fabrics.

Wash-fastness

Table III shows the physical properties of the treated fabric after it had been washed 20 times. The washed fabric showed decreased antiwrinkle properties, strength, and UV light resistance. Some of the crosslinking was damaged, and some of the medical agents had been washed away. The traditionally treated fabric showed a 4% decline in DCRA and WCRA, while the fabric treated with the mixed sol showed a 6% decline in antiwrinkle properties. In addition, the former declined in strength by 3.5%, while the latter declined in strength by about 5.5%. This showed that the agents in the fabric treated with the mixed sol

TABLE III
Washing Fastness of Treated Fabrics

		Properties					
TEOS/TTB mole ratio	Washing times	DCRA (W : F)°	WCRA (W : F)°	TSR (%)	Softness (cm)	Yellowing index	Transmittance (%)
0/0 (no added)	0	287	254	47.7	4.8	4.8	5.08
	20	276	248	45.9	4.2	4.7	5.13
5.0/1.0	0	299	274	51.1	5.2	4.2	0.18
	20	281	257	48.2	4.4	4.0	1.04

were washed away. However, although the fabric treated with the mixed sol showed a significant decline in physical properties after being washed 20 times, it remained superior to the traditionally treated fabric in all properties except softness.

CONCLUSIONS

In this experiment, DMDHEU was applied to a cotton fabric, and different mole ratios of TEOS/TTB were added. Then, the mixture underwent a process of immersion, padding, drying, and curing. This research explored the effect of a mixed sol on the chemical and physical properties of the treated fabric. The following conclusions were reached. First, as confirmed by FTIR and NMR tests, hydrogen bonds had formed between SiO_2 and DMDHEU. Second, the treated fabric showed improved antiwrinkle properties, strength retention, and yellowing when the mole ratio of TEOS was increased, whereas the softness showed the opposite trend; however, when the mole ratio of TEOS/TTB was set at 10/1, the fabric was weakened in terms of its antiwrinkle properties. Third, the fabric treated with TEOS/TTB was superior to the traditionally treated fabric in terms of UV light resistance. Fourth, when the mole ratio of TEOS/TTB was 2.5/1 or 5.0/1, and 10% DMDHEU was added during the fabric treatment, followed by drying for 5 min at 80°C and curing at 150°C for 2 min, the fabric had better and more balanced physical properties.

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