Application of DMEU/SiO$_2$ Gel Solution in the Antiwrinkle Finishing of Cotton Fabrics

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ABSTRACT: In this experiment, cotton fabrics were treated by padding, drying, and curing with an antiwrinkle finishing reagent, dimethylolethylene urea (DMEU), in combination with different concentrations of tetraethoxysilane (TEOS) and isopropanol (IPA) at various volumes. The treated fabrics were studied to determine the effects of adding TEOS and IPA. They were also analyzed using Fourier transform infrared (FTIR) and nuclear magnetic resonance (NMR) methods to examine the binding between SiO$_2$ and DMEU. The results showed that hydrogen bonds formed between SiO$_2$ and DMEU. TEOS was found to improve the antiwrinkle properties, tensile strength retention, and yellowing of the treated fabrics, although their softness was slightly reduced. The solvent IPA was shown to decrease the tensile strength of treated fabrics, although it improved their antiwrinkle properties. We observed only one stage of pyrolysis in untreated cotton fabrics, whereas the treated fabrics showed two stages. In addition, the fabrics treated with TEOS showed improved heat resistance. Our findings demonstrated that cotton fabrics showed excellent antiwrinkle properties and high tensile strength, when treated with a finishing solution composed of DMEU, 3% TEOS, IPA and water, followed by predrying and curing. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 4136–4143, 2006

Key words: strength; fibers; Fourier transform infrared; nuclear magnetic resonance; pyrolsis

INTRODUCTION

As the quality of life of individuals increases so does the demand for higher quality clothing. People are concerned not only with the appearance of their clothes but also with their functionality. Therefore, the question of how to produce multifunctional fabrics has been 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 will increase their value, which will have a huge economic impact. Nanotechnology is currently applied in the development of ultraviolet light resistance, antistatic properties, infrared light resistance, antibacterial properties, and water and oil repellent.[1–7] 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.

Gel solution (sol) is a medium in which 1–100-nm particles (basic units) are dispersed, whereas 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.[8]

During the finishing process for cotton fabrics, the crosslinking reagent forms links between fiber molecules, which consequently become firm and straight.[9,10] However, the acidic catalyst tends to degrade fibers at high temperatures, leading to a substantial loss of tensile strength.[11–14] The sol–gel method utilizes metallic alkoxides as precursors, which can be hydrolyzed under mild conditions and polymerize to a gel solution. The solvent is then 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.[15] For example, 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. The particles of the original nanogel solution form a three-dimensional reticular structure, which can further increase the tensile strength of the fabric.

As it is easy to change the chemical and physical properties of nanogel solutions, we previously showed that using different types of nanogel solution makes it possible to improve the wearing functions of fabrics and to increase the value of textiles.[16] There are few research reports on the application of the Sol–gel technique in fabrics. However, according to its basic principles, it should be feasible and worthwhile to apply this technique to produce functional textile products. The postfinishing method plays an important role in giving textiles their functional properties. This technique is simple and effective without the need to change the original production methods and facilities. By adding the appropriate functional materials during the postfinishing stage, we can obtain textiles with the required functions. This approach is suitable for manufacturing functional products in a variety of forms and in small quantities.

EXPERIMENTAL

Materials

The chemicals used were as follows: paraformaldehyde (PF; research grade; FERAK); ethylene urea (EU) and tetraethoxysilane (TEOS, both research grade; ACROS); isopropanol (IPA, research grade; Panreacquimicasa); hydrochloric acid, sodium polyphosphate, sodium lauryl sulfate (SDS), and methanol (all research grade, purchased from Wako Pure Chemical Industry, Japan) and softener (Ailigen; provided by BASF). The specifications of the cotton fabrics before finishing were $32^S \times 32^S$ ends (100) and picks (56) (supplied by the Yi Hwa Textile).

Methods

Dimethylolethylene urea preparation

Dimethylolethylene urea (DMEU) was synthesized according to the Hoover method.[17] PF and EU were weighted in a molar ratio of 2.1:1 as follows: 1.5 mol EU was dissolved in 125 mL methanol in a reaction trough, and 3.15 mol PF was dissolved in 125 mL methanol, followed by the addition of 1 g NaOH. The solution was stirred and heated to 40°C until it became clear. The clear solution was poured into the reaction trough and allowed to react at 70°C for 1 h. The reaction solution was then filtered and stored in a refrigerator until it had cooled and crystallized. The resultant crystal was rinsed and recrystallized in methanol. Finally, the crystal was dried in a vacuum oven.

Preparation of mixed gel solution

Initially, 10 g DMEU was dissolved in 20 mL water and stirred evenly. An appropriate amount of TEOS was then dissolved and stirred evenly in 45 or 15 mL IPA and 2.5 mL of 0.05N HCl. These solutions were prepared at room temperature and stirred for 2 h until they became a mixed liquid gel. To produce composites, the liquid gel was poured into Petri dishes and placed in a vacuum oven to remove the IPA. These composite samples were used for the subsequent tests.

Antiwrinkle finishing of cotton fabrics

The finishing solution contained 10% mixed liquid gel, 1% sodium hypophosphate, and 1% softener. The cotton fabric was soaked in the finishing solution, using the alternate dipping and padding method (with a pick-up of 85%). Following predrying for 5 min at 80°C and curing at different temperatures (130–170°C) and for various time periods (30–180 s), the treated fabrics were washed in a solution containing 2% soap, rinsed in water, dried, sealed in bags, and placed into a drying machine to prepare them for the physical property tests.

Analysis and examination of treated fabrics

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 internal reflectance element. 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 of 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, and the spectra were observed under crosspolarization, magic angle sample spinning, and power decoupling conditions with a 90° pulse and 4-s cycle time. The thermal resistance of samples was measured by DuPont 2200 weight-loss analyzer. The 5–10 mg samples were placed in alumina crucibles and tested with a thermal ramp over a temperature range of 30–600°C, at a heating rate of 20°C/min under nitrogen flow speed of 20 cc/min, after which their initial decomposition temperature (IDT) was obtained. The dried and wet antiwrinkle angles of the treated fabrics were measured according to method ASTM D 1295–67 (Monsanto, 1975). The yarn tensile strength was measured by an Alphaten 400 pull tester, according to method ASTM D1682–64. 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 on the wash fastness properties were performed at 40°C, using a Rapid H-Type laboratory dyeing machine. As washing solution, 1% aqueous solution of sodium lauryl sulfate (SDS) with pH 7 was used. After a leaching of 20 min, the textile samples were rinsed intensively
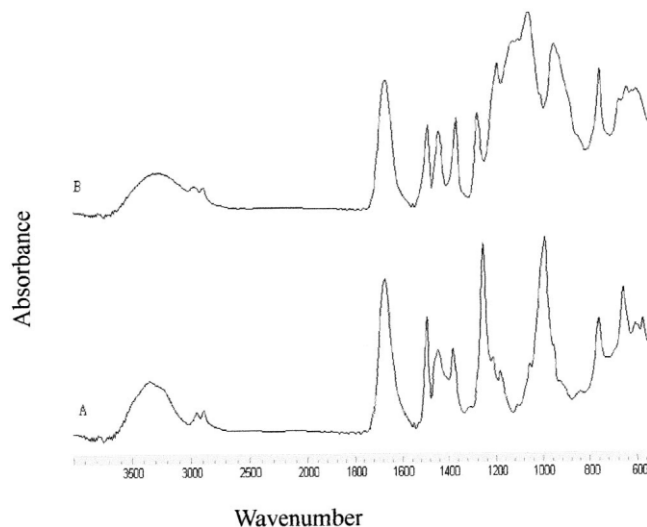
Figure 1 FTIR of DMEU and DMEU/SiO$_2$ hybrid material. (A, DMEU; B, DMEU/SiO$_2$).
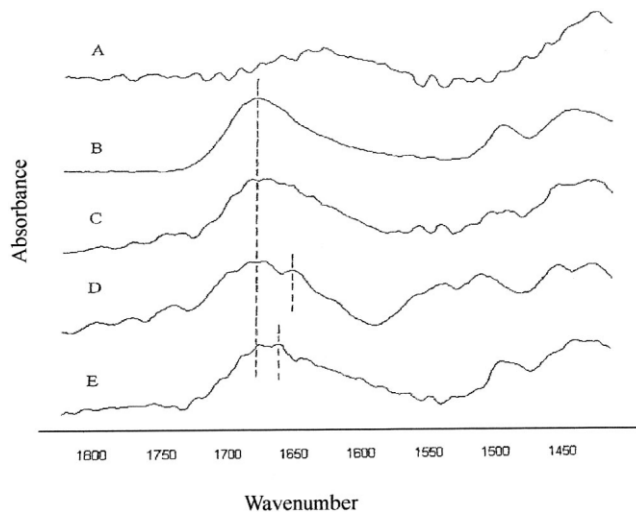

Figure 2 FTIR of treated fabric. [A, raw fabric; B, treated with DMEU; C, with (DMEU + 1% TEOS); D, with (DMEU + 3% TEOS + 45 mL IPA); E, with (DMEU + 3% TEOS + 15 mL IPA)]

with water, dried at room temperature, and physical properties were again investigated after 20 times wash.

RESULTS AND DISCUSSION

FTIR analysis of treated fabrics

To analyze the reaction between DMEU and SiO$_2$ in the finishing solution, an aliquot of the mixed solution was heat concentrated and examined by FTIR analysis. In Figure 1(A), the peak at 3418 cm^{-1} represents the absorbance of the —OH of DMEU, whereas that at 1682 cm^{-1} represents the absorbance peak of the >C=O functional group. When DMEU reacted with SiO$_2$, the original —OH absorbance peak of DMEU shifted to 3318 cm^{-1} and the absorbance peak of the >C=O functional group shifted to 1669 cm^{-1}. A broad absorbance peak appeared at 1090–1060 cm^{-1}, which belonged to Si—O—C [Fig. 1(B)]. These findings suggested that DMEU formed partial hydrogen bonds and covalent bonds with SiO$_2$. Figure 2(A) indicates the experimental data for untreated cotton fabrics, in which there is no absorption peak of >C=O at the 1700 cm^{-1} or so. The FTIR results for the fabrics treated with DMEU using a conventional method are shown in Figure 2(B). The most significant change was that an absorbance peak occurred at 1678 cm^{-1}, which represented the absorbance of the >C=O group of DMEU. Several conclusions can be drawn from these findings. First, when TEOS was included in the finishing procedure, the absorbance peak of the >C=O functional group clearly shifted towards the low frequency area at 1678 cm^{-1}. When TEOS was added at a higher concentration, the shift became greater as shown in Figures 2(C) (1% TEOS) and 2(D) (3% TEOS),

at 1670 and 1651 cm^{-1}, respectively. This was due to the fact that when the fibers were etherified with DMEU, the >C=O functional group of DMEU formed hydrogen bonds with the —OH base of SiO$_2$. This result was similar to many reports published previously.[18–20] Second, when the finishing solution contained the solvent IPA, the absorbance peak of >C=O (shown in [Fig. 2(B)]) also significantly shifted towards the low frequency area; when a higher vol-
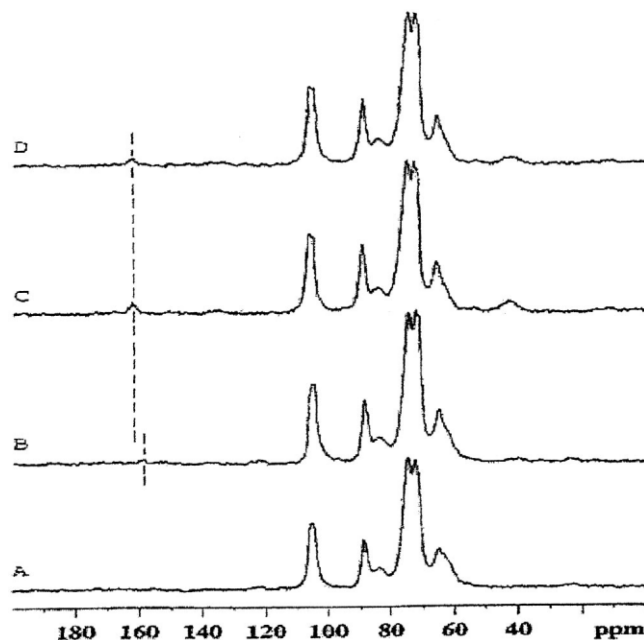

Figure 3 ^{13}C NMR of treated fabrics. [A, raw fabric; B, treated with DMEU; C, added 1% TEOS (water/IPA = 55/45); D, added 3% TEOS (water/IPA = 55/45)]
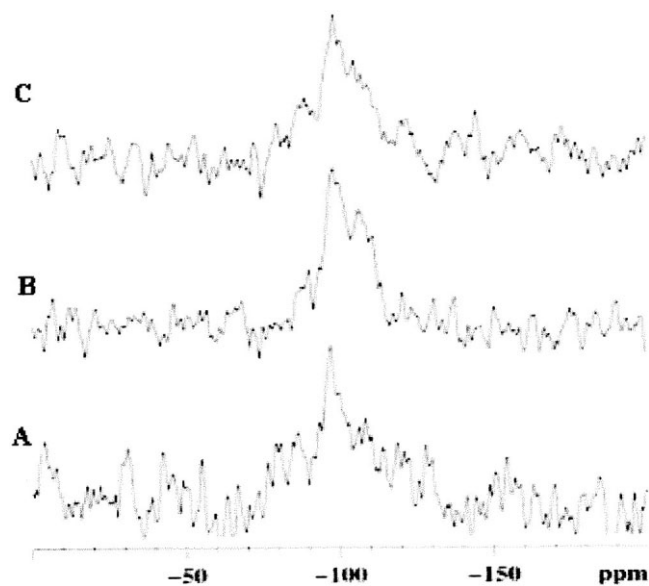
Figure 4 ^{29}Si NMR of treated fabrics. [A, added 1% TEOS (150°C); B, added 3% TEOS (150°C); C, added 3% TEOS (170°C)]

ume of IPA was added, the shift was larger, as shown in Figures 2(D) (45 mL IPA) and 2(E) (15 mL IPA), at 1651 and 1669 cm^{-1}, respectively. This was because the solvent diffused into the fibers, which then expanded. It was advantageous for the fibers to have a crosslinking reaction to the finishing reagent.

NMR

Because the absorbance peaks of Si—O—Si or Si—O—C overlapped with the absorbance peak of C—O—C, it was difficult to distinguish them. Thus, it was necessary to test whether ^{29}Si was present using NMR.

Figure 3(A) shows the control untreated fabrics, which had no absorbance peak at 160 ppm because the cotton fibers contained no >C=O functional group. However, when the fabrics were treated with DMEU, the crosslinking reaction between the DMEU and the fibers caused an absorbance peak at 160.8 ppm, which was attributed to the >C=O of DMEU [Fig. 3(B)]. Furthermore, the addition of 1 or 3% TEOS during the

TABLE I
Properties of Treated Fabrics that were Finished with DMEU[a] by Sol–Gel Method

Processed methods[b]	Curing temperature (°C)	TSR (%)	DCRA (W + F)°	WCRA (W + F)°	Softness (cm)	Yellowing index
	130	64.3	254	230	5.6	3.3
	140	56.7	276	247	5.5	3.4
	150	54.3	295	258	5.4	3.5
	160	50.1	297	263	5.5	3.6
A	170	48.3	300	270	5.5	3.5
	130	55.6	273	246	5.0	2.9
	140	50.2	286	261	5.1	3.1
	150	46.1	305	273	5.1	3.3
	160	43.7	310	280	5.3	3.4
B	170	41.5	313	286	5.3	3.4
	130	70.7	280	252	5.8	2.5
	140	66.9	291	265	5.9	2.6
	150	63.5	308	284	6.1	2.7
	160	56.4	314	287	6.1	2.6
C	170	52.2	316	292	5.7	3.0
	130	72.5	266	238	5.8	3.0
	140	68.3	280	252	5.6	3.1
	150	64.7	295	260	5.5	3.1
	160	57.9	299	268	5.7	3.6
D	170	54.7	302	275	5.4	3.7
	130	58.4	273	243	5.7	3.3
	140	53.3	284	257	5.8	3.1
	150	49.0	299	265	6.1	3.0
	160	46.1	304	274	5.7	3.1
E	170	43.5	307	281	6.1	3.0

[a] Ten percent DMEU, 1% MgCl$_2$, and 1% softening agent.
[b] A: DMEU (solvent is H$_2$O, A method) (pad→dry:80°C × 5′→cure: 150°C × t'); B: DMEU (H$_2$O/IPA, v/v = 55/45, B method); C: DMEU + 3% TEOS (H$_2$O/IPA, v/v = 55/45, C method); D: DMEU + 3% TEOS (H$_2$O/IPA, v/v = 85/15, D method); E: DMEU + 1% TEOS (H$_2$O/IPA, v/v = 55/45, E method).

<div align="center">TABLE II
Properties of Treated Fabrics that were Finished with DMEU[a] by Sol–Gel Method</div>

Processed methods[b]	Curing time (s)	Properties				
		TSR (%)	DCRA $(W + F)°$	WCRA $(W + F)°$	Softness (cm)	Yellowing index
Greige fabric		100	156	134	5.2	2.3
	30	70.7	257	236	5.4	3.4
	90	65.9	271	247	5.7	3.4
A	180	54.3	295	258	5.4	3.5
	30	59.4	272	251	5.0	3.1
	90	52.9	291	265	5.1	3.2
B	180	46.1	305	273	5.1	3.3
	30	71.2	280	259	6.0	2.8
	90	68.1	296	270	5.9	2.7
C	180	63.5	308	284	6.1	2.7
	30	73.9	265	240	5.6	3.0
	90	71.1	284	254	5.6	3.2
D	180	64.7	295	260	5.5	3.1
	30	57.4	268	247	5.5	2.5
	90	52.2	287	258	5.9	2.9
E	180	49.0	299	265	6.1	3.0

[a] Ten percent DMEU, 1% $MgCl_2$, 1% softening agent.
[b] A: DMEU (solvent is H_2O, A method) (pad→dry:80°C × 5′→cure:150°C × t'); B: DMEU (H_2O/IPA, v/v = 55/45, B method); C: DMEU + 3% TEOS (H_2O/IPA, v/v = 55/45, C method); D: DMEU + 3% TEOS (H_2O/IPA, v/v = 85/15, D method); E: DMEU + 1% TEOS (H_2O/IPA, v/v = 55/45, E method).

antiwrinkle finishing of cotton fabrics led to absorbance peaks of $>C\!\!=\!\!O$ at 162.3 and 162.8 ppm [Figs. 3(C) and 3(D)]. This indicated that when TEOS was added, it produced SiO_2 through hydrolysis and polymerization, which linked to the $>C\!\!=\!\!O$ of DMEU by hydrogen bonding, so that its absorbance tended to shift towards the high frequency area.[21–23] However, variation in the TEOS concentration did not significantly influence the shift of absorbance.

In terms of ^{29}Si NMR, Figure 4(A) illustrates that in fabrics treated with 1% TEOS and DMEU, Si was observed at −42.50 and −96.86 ppm after Q_1 and Q_3 hydrolysis, respectively. Figure 4(B) shows that Si was observed at −89.71 and −97.66 ppm, and at −105.78 and −120.41 ppm, after Q_3 and Q_4 condensation, respectively. Figure 4(C) illustrates that Si was observed at −88.51 and −98.08 ppm, and −106.72 and −121.48 ppm, after Q_3 and Q_4 condensation, respectively. These results confirm that the fabrics treated with TEOS and DMEU contained Si. In addition, Q_3 and Q_4 condensation were more obvious when the finishing temperature or TEOS concentration was higher. This improved the reticular structure of the fibers, which in turn improved the tensile strength of the fabrics.

Influence of finishing temperature

Table I illustrates that the tensile strength–retention rate of the treated fabrics gradually decreased when the finishing temperature increased, because the higher finishing temperature had greater oxidative effects on the fabrics, and the enhanced crosslinkage in the treated fabrics tended to concentrate the stress. Furthermore, the dried antiwrinkle angle of the treated fabrics increased gradually as the finishing temperature increased. As a result, more crosslinked chains formed, giving better antiwrinkle properties.
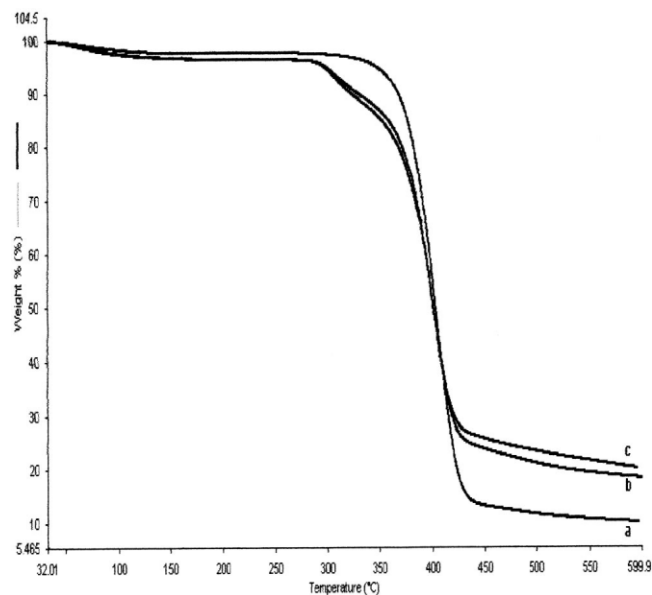

Figure 5 TGA of treated fabrics. [A, raw fabric; B, with DMEU; C, added 1% TEOS (water/IPA = 55/45)]

TABLE III
Thermoresistance of Treated Fabrics[a]

	Properties		
Processed conditions	Initial decomposition temperature[b] (°C)	Decomposition rate (%/°C)	Remnant[c] (%)
Greige	370.31	−1.6295	11.46
Processed methods[d]			
A	376.14	−1.3283	20.85
C	379.63	−1.1952	23.12
D	379.12	−1.2074	22.58
E	378.72	−1.2413	22.35
Processed temperature (°C)			
130	377.54	−1.2947	21.55
150	379.63	−1.1952	23.12
160	379.52	−1.1944	24.15
170	379.93	−1.1931	24.97

[a] Processed time is 3 min.
[b] It is the second step decomposition temperature except the greige fabric.
[c] Remnant is the percentage that remains after the temperature reaches 500°C.
[d] Same as Table I.

The wet antiwrinkle angle showed a similar trend. Table I showed that there was no significant relationship between the finishing temperature and the softness of the treated fabrics. Unlike the fabrics treated at 130°C, which showed improvements in terms of yellowness, the fabrics treated at 150, 160, and 170°C showed no significant relationship between yellowness and temperature.

Influence of finishing methods

Table I shows that the finishing method was related to the physical properties of the treated fabrics. The tensile strength–retention rates of the treated fabrics were as follows: 3% TEOS in 15 mL solvent (D) >3% TEOS in 45 mL solvent (C)> traditional finishing in water (A) >1% TEOS in 45 mL solvent (E) >45 mL IPA added to the traditional finishing in water (B). This pattern suggested that the added solvent had harmful effects on the tensile strength of the treated fabrics, whereas the combined treatment with TEOS had beneficial effects on tensile strength. The former effect was due to the diffusion of IPA into the fibers, which caused them to expand. This was particularly obvious in the absence of TEOS, when the tensile–strength differences between the fabrics treated by methods A and B were clearly visible. However, this situation was altered when TEOS was included in the finishing process. The tensile strength of the treated fabrics increased following the addition of TEOS. Moreover, when TEOS was added at a higher concentration, the tensile strengths of the fabrics were improved. This was because the TEOS was hydrolyzed and polymerized in the reaction process to produce SiO_2, the residual —OH base, which not only etherified with the

fibers but also bound the $>C=O$ functional group of DMEU. Therefore, TEOS increased both the heat resistance and the tensile strength of the fibers.

The order of the dried antiwrinkle angles was C > B > E > D > A. This was because adding IPA led to a more significant expansion of the fibers, which was advantageous for the formation of crosslinkages. In addition, extra TEOS formed a superior SiO_2 reticular structure inside the fiber molecules, which increased the dried antiwrinkle angle of the fabric.

Influence of finishing time

In industrial applications, the curing conditions for the antiwrinkle finishing of cotton fabrics are generally 150°C for 2 min. Thus, the present experiment used this temperature to study, further, how the curing time affected the physical properties of treated fabrics. The results shown in Table II demonstrate that regardless of the finishing method, the tensile strength of the treated fabric was significantly decreased if the curing period was extended. A similar trend was seen for the antiwrinkle angle, as a longer curing time caused increased crosslinkage between the fibers and chemicals, although the curing time had less significant effects on yellowness and softness.

TGA

Untreated cotton fabrics have only one stage of decomposition (Fig. 5) compared with treated fabrics which have two stages (lines b and c in the figure). The first stage involved the decomposition of incompletely reacted finishing reagent, whereas the second stage

TABLE IV
Wash Fastness on the Physical Properties of Treated Fabrics[a]

Processed methods[b]	Washing times	Properties				
		TSR (%)	DCRA (W + F)°	WCRA (W + F)°	Softness (cm)	Yellowing index
	0	54.3	295	258	5.4	3.5
A	20	53.8	286	249	5.0	3.3
	0	64.7	295	260	5.5	3.1
D	20	62.9	283	250	4.9	3.0

[a] Curing condition, 150°C × 3′.
[b] A: DMEU (solvent is H_2O, A method) (pad→dry: 80°C × 5′→cure: 150°C × t'); D: DMEU + 3% TEOS (H_2O/IPA, v/v = 85/15, D method).

involved the decomposition of treated fabrics. The data in Table III indicate that after finishing, the cotton fabrics showed a decrease in the initial decomposing temperature, the rate of decomposition slowed, and the residual amount of decomposition at 500°C significantly increased. This was because the fibers expanded during the finishing process and were hydrolyzed and oxidized by acids, which led to a decrease of the initial decomposing temperature. However, soon afterwards, because of the presence of intramolecular crosslinking chains, the fibers became more difficult to break down and the decomposition rate slowed. After finishing, the heat resistance of the fabrics increased, which was similar to the results of previous studies.[24]

Comparing the effects of various finishing methods on the heat resistance of fabrics, as shown in the Table III, it was clear that, with the exception of method A, the fabrics treated by all of the methods showed similar heat resistance. The fabrics treated by method A had no SiO_2 reticular structure in the fiber molecules. The heat resistance of the various fabrics treated by method C at different temperatures is shown in Table III. The fabrics treated at 130°C showed the poorest heat resistance, because at this temperature, the reaction between the fiber molecules and the finishing reagent was incomplete, and so the crosslinkage inside the fiber molecules was weaker. This was confirmed by the physical properties of the treated fabrics.

Wash fastness

From Table IV, the crosslinking part in the fiber of the treated fabrics by D method treating was broken after washing 20 times leading to reducing its antiwrinkle angle about 4%. Compared to traditional method, its antiwrinkle angle decreased slightly. However, the tensile strength and softness of the treated fabrics by D method treating is better than that by traditional method.

CONCLUSIONS

This experiment employed the DMEU antiwrinkle finishing reagent combined with different concentrations of TEOS or different volumes of IPA to process cotton fabrics using traditional methods, such as soaking, pressing, absorption, predrying, and curing, and studied how TEOS affected the physical properties of the treated fabrics. On the basis of the experimental results, we can draw the following conclusions

1. Adding TEOS has a beneficial effect on the antiwrinkle properties, tensile strength, and yellowness of fabrics, but has a slight negative effect on the softness of the treated fabrics.
2. Adding the solvent IPA is harmful to the tensile strength of treated fabrics but improves the antiwrinkle properties.
3. Untreated fabrics only undergo one stage of decomposition, whereas treated fabrics undergo two stages. Fabrics that are treated by traditional methods using DMEU are the only ones to show good heat resistance.
4. Fabrics that are treated in DMEU with a combination of 3% TEOS and a small amount of the solvent IPA by soaking, pressing absorption, predrying, and curing show improved antiwrinkle properties and tensile strength.

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