

Grafting Polymerization of 2-[3-(2*H*-Benzotriazol-2-yl)-4-hydroxyphenyl]ethyl Methacrylate on Vinyltriethoxysilane-Treated Cotton for the Preparation of Ultraviolet-Protective Fabrics

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ABSTRACT: Vinyltriethoxysilane was used to modify the surface of cotton to provide polymerizable vinyl groups on the fiber surface. An ultraviolet-absorbing monomer, 2-[3-(2*H*-benzotriazol-2-yl)-4-hydroxyphenyl]ethyl methacrylate, was polymerized on the vinyltriethoxysilane-treated fabric to prepare ultraviolet-protective cotton. The effects of the amounts of the solvent, silane coupling agent, and 2-[3-(2*H*-benzotriazol-2-yl)-4-hydroxyphenyl]ethyl methacrylate on the surface morphology and ultraviolet-protection factor of the treated cotton fabric were investigated. With a suitable

process, poly{2-[3-(2*H*-benzotriazol-2-yl)-4-hydroxyphenyl]ethyl methacrylate} was successfully coated onto the fabric, and it significantly reduced ultraviolet transmission through the fabric, resulting in a cotton fabric with excellent ultraviolet-protection properties. The use of a silane coupling agent helped to ensure a polymer coating with good uniformity and good resistance to washing. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 62–69, 2009

Key words: coatings; fibers; graft copolymers; thin films

INTRODUCTION

Silane coupling agents have been widely employed for surface modification. They are often used to improve the adhesion between a polymer matrix and reinforcements.¹ The general formula of organosilanes is $\text{RSi}(\text{OR}')_3$, where R and R' represent organofunctional and hydrolyzable groups, respectively. Vinyltriethoxysilane (VTES), which is relatively inexpensive, has been used to modify glass surfaces to improve scratch protection² and to functionalize mesoporous silica.³ Recently, silane coupling agents containing polymerizable groups such as VTES and 3-methacryloxypropyl trimethoxysilane have been used to modify substrates that were subsequently grafted by polymerization. The treated substrates, such as glass fibers,⁴ alumina,⁵ silica,⁶ and TiO_2 ,^{7,8} are mostly used as reinforcements in polymer composites or nanocomposites. However, there has been no study of the use of this technique to modify a

cotton fabric. In general, grafting polymerization on cellulose includes (1) grafting by free-radical polymerization, (2) grafting with the help of condensation or addition reactions, and (3) grafting initiated by ionic polymerization.⁹ Some of these processes are complicated and require many reaction steps. This work introduces a simple process for the grafting of a vinyl monomer onto cotton fabric.

The ultraviolet (UV)-protective properties of clothing have received much attention in recent years because of the hazardous effects of UV radiation on human skin. The factors affecting the extent of protection rendered by clothing have been reported.^{10–13} The change in sun exposure habits over the past few decades and the increase in the incidence of skin cancer are some of the reasons that UV-protective properties of fabrics have become more important. To enhance the UV protection of textiles, UV absorbers are applied to fabrics by various methods such as the addition of UV absorbers during the dyeing process^{14,15} and the synthesis of dyes with UV absorbers.¹⁶ UV absorbers have also been used as photostabilizers for cellulosic fibers to protect fabrics from UV degradation.¹⁷ In this study, an organic monomer containing a UV-absorbing system was applied to cotton pretreated by VTES via graft polymerization. The monomer, 2-[3-(2*H*-benzotriazol-2-yl)-4-hydroxyphenyl]ethyl methacrylate (BEM), was used in this study because of the strong

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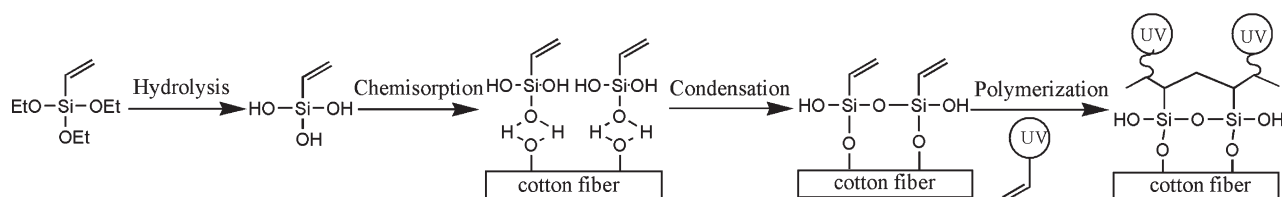


Figure 1 Reaction scheme of grafting polymerization.

photostability of benzotriazole.¹⁸ Benzotriazole, with an intramolecular hydrogen bond in its structure, strongly absorbs UV radiation and rapidly dissipates the energy through a mechanism that involves the reversible rearrangement of a six-membered, intramolecularly hydrogen-bonded ring. Thus, the molecule remains chemically unchanged and is able to undergo a large number of activation–deactivation cycles. This property helps to ensure that BEM will be able to retain its UV-absorbing capability for a very long time.

The chemical reactions employed in this study are depicted in the schematic shown in Figure 1. In the reaction, VTES reacted at the hydrolyzed silicon orthoester functionality with cotton and at the vinyl group with the monomer containing the UV-absorbing system. The ethoxy groups in VTES were first hydrolyzed into silanol groups, which then formed hydrogen bonds with the hydroxyl groups of the cellulose molecules on the cotton surface. The condensation reaction occurred when the fabric was dried, leading to covalent bonding between the silane and cotton. After this, the vinyl groups of VTES were allowed to react with the BEM monomer through a polymerization reaction resulting in a thin UV-absorbing film coated on the fiber surface. The UV-protection properties of the treated fabric were then studied, and its surface before and after the treatment was characterized with scanning electron microscopy (SEM) and Fourier transform infrared/attenuated reflection spectroscopy (FTIR–ATR).

EXPERIMENTAL

Materials

A plain-weave, medium-weight (150 g/m²) cotton fabric was purchased from Boonchay Co., Ltd. (Bangkok, Thailand). The fabric was desized, scoured, and bleached at the factory. Before use, the fabric was washed in a washing machine at 95°C several times until it was free from any remaining surfactant.

BEM, VTES (97%), and acetic acid (99.7%) were purchased from Aldrich Co. (St. Louis, MO). Ammonium persulfate (99%) was purchased from Asia Pacific Specialty Chemicals, Ltd. (New South Wales, Australia). Dimethylacetamide (DMAC; 99.5%) was

purchased from Labscan Co. (Dublin, Ireland). All chemicals were used without further purification.

Modification of the cotton fabric by VTES–BEM

VTES was hydrolyzed in an aqueous solution in the concentration range of 1–15 vol %. The pH of the silane aqueous solution was adjusted to 4 with acetic acid. The hydrolyzation was carried out at room temperature for 2 h. After the VTES was completely hydrolyzed, the solution became homogeneous. A 6.5 cm × 6.5 cm piece of cotton fabric weighing 0.73 g was soaked in the silane solution at the required concentration for 24 h at room temperature. The ratio of the fabric to the solution was 1 : 20. The pH of the treating solution was kept at 4 because hydrolyzed VTES has maximum stability at this pH.¹ In a previous work,¹⁹ Weeding et al. found that, with 1 h of drying at 100°C, covalent bonding between the silane coupling agent and glass microsphere was proved to have occurred by ²⁹Si-NMR. In this work, the obtained fabrics were heated in an oven for 5 h at 120°C to allow condensation of the adsorbed silane to occur.

Polymerization of BEM on cotton was carried out in a 40-mL vial containing a 6.5 cm × 6.5 cm piece of untreated or VTES-treated cotton fabric, BEM (with the concentration varied from 1.0 to 10.0 mM), and ammonium persulfate at 70°C. Ammonium persulfate was used to initiate the polymerization at the initiator/monomer molar ratio of 1 : 2. BEM and ammonium persulfate were dissolved in a mixture of water and DMAC. In a total volume of 35 mL, the amount of DMAC was varied from 5 to 30 mL so that we could study its effect on the coated film. After 15 h of polymerization, the fabric was taken out from the vial and placed in an oven at 90°C until it was dry. After that, it was washed with water and dried once again.

Characterization of the treated cotton surface

SEM (JSM 5200, JEOL, Tokyo, Japan; 15 kV) was used to study the surface morphology of the coated fabric. FTIR–ATR with a ZnSe plate was used to analyze the chemical groups present on the cotton surface. The spectrometer was a Nexus 670 spectrometer (Nicolet, Madison, WI), and 32 scans were

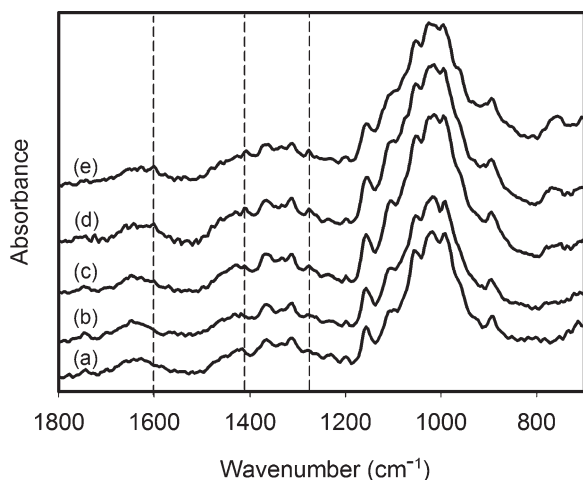


Figure 2 FTIR-ATR spectra of (a) untreated cotton and (b-e) silane-treated cotton (1, 5, 10, and 15 vol %, respectively).

taken at a 4-cm^{-1} resolution in the frequency range of $4000\text{--}400\text{ cm}^{-1}$. The water contact angles of the treated surface were measured with a Krüss DSA 10-Mk2 contact-angle-measurement instrument (Hamburg, Germany). A water droplet with a volume of $10\text{ }\mu\text{L}$ was placed on the tested surface, and the dynamic contact angles of the droplet were measured after 15 and 25 s.

Determination of the UV-protection properties of the treated fabric

The determination of the UV-protection properties of the treated fabric was based on AATCC Test Method 183-2004.²⁰ The UV transmission of the fabric was measured with a Shimadzu 2550 UV spectrophotometer (Kyoto, Japan) with the ISR-2200 integrating sphere attachment. The transmittance percentage for wavelengths ranging from 280 to 400 nm was measured in intervals of 2 nm. Three measurements of the UV transmittance were performed for each specimen in the warp, weft, and diagonal directions. The results were the mean values of the three measurements from duplicate specimens. The data were then used to calculate the ultraviolet-protection factor (UPF) of the fabric.

Washing tests of the treated fabrics

The durability of the UV-protection properties of the treated fabrics was determined with washing tests. Fabrics treated with various amounts of VTES and BEM were washed 4 times (30 min per time) in water in a Daelim DL-6000 dyeing machine (Gyeonggi-do, Korea) at 90°C and a speed of 30 rpm

with a fabric/water ratio of 1 : 100, the UPF of the fabric being determined after each wash.

RESULTS AND DISCUSSION

Characterization of the treated fabric surface by FTIR-ATR

The presence of vinyl functional groups on the cotton surface after VTES treatment was confirmed by FTIR-ATR. The absorption peaks assigned to VTES are shown in Figure 2. The peak at 1600 cm^{-1} is assigned to C=C stretching. The peak around 1400 cm^{-1} is assigned to C-H in-plane deformation of $=\text{CH}_2$. The peak at 1274 cm^{-1} is due to $\text{CH}=\text{CH}_2$ in-plane bending.²¹ When the amount of VTES used in the silane treatment increased, the characteristic peaks of the vinyl groups appeared with higher intensity, thus confirming that VTES had been successfully attached to the fabric surface. To further confirm the covalent bond formation between VTES and cotton, a subtraction spectrum of VTES-treated and untreated cotton spectra over the wavelength range of $1300\text{--}1000\text{ cm}^{-1}$ was obtained, as shown in Figure 3. The subtraction spectrum shows the peak of Si-O-C around 1190 and 1089 cm^{-1} , which confirms the occurrence of a condensation reaction between the silane coupling agent and cotton.²² The spectrum also shows peaks at 1134 and 1038 cm^{-1} belonging to the Si-O-Si bond, further confirming the presence of the silane on the fiber surface.

After the silane treatment, the vinyl groups of the silane were polymerized with BEM, which is a vinyl monomer containing a UV-absorbing unit. Figure 4 compares the FTIR-ATR spectra of the untreated cotton, 5 vol % VTES-treated cotton, and 5 vol % VTES/6.0 mM BEM-treated cotton. From the spectra, additional peaks of BEM can be seen at 1517

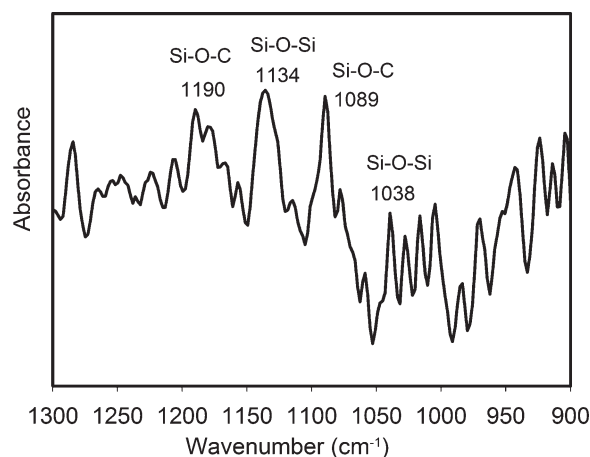


Figure 3 FTIR subtraction spectrum of the spectra of VTES-treated and untreated cotton.

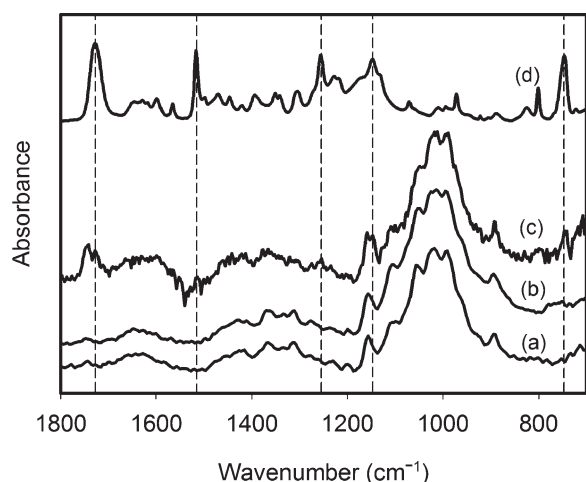


Figure 4 FTIR spectra of (a) untreated cotton, (b) 5 vol % VTES-treated cotton, (c) 5 vol % VTES/6.0 mM BEM-treated cotton, and (d) poly(BEM).

(assigned to C=C of the substituted benzene ring) and 1730 cm^{-1} (assigned to C=O stretching). In addition, there are peaks at 1250 and 1150 cm^{-1} due to C–O stretching of ester and a peak at 745 cm^{-1} due to C–H out-of-plane bending of the benzene ring of benzotriazole.²¹ The observed characteristic peaks of poly[2-[3-(2H-benzotriazol-2-yl)-4-hydroxyphenyl]ethyl methacrylate] [poly(BEM)] confirmed that poly(BEM) was successfully coated on the cotton surface.

Characterization of the treated fabric surface by contact-angle measurements

The existence of vinyl groups on the cotton surface was observed indirectly with measurements of the water contact angles. Normally, a water droplet will disappear immediately on untreated cotton because of the hydrophilicity of its hydroxyl groups. Table I shows the contact angles of VTES-treated and

TABLE I
Water Contact Angles of VTES-Treated and VTES/BEM-Treated Cotton

VTES (vol %)	BEM (mM)	Contact angle at 15 s	Contact angle at 25 s
5%	—	138.3	134.9
10%	—	146.5	144.7
15%	—	150.9	150.5
5%	2.0	127.1	— ^a
10%	2.0	125.7	— ^a
15%	2.0	105.1	— ^a

^a The water droplet disappeared before the time reached 25 s.

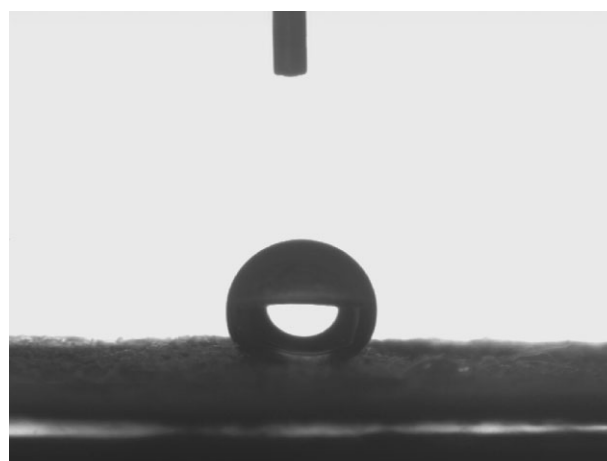


Figure 5 Water droplet on 15 vol % VTES-treated cotton at 25 s.

VTES/BEM-treated cotton as measured by the sessile drop method. The contact angles of VTES-treated cotton after 25 s were in the range of 134.9–150.5°, much higher than 90°, and the greater the amount of VTES was, the higher the contact angle was. The results thus showed that the presence of vinyl groups changed the cotton surface from a hydrophilic surface to a hydrophobic surface. This is clearly confirmed by Figure 5, which shows a water droplet on the VTES-treated cotton surface still retaining its nearly spherical shape even after 25 s.

In the case of VTES/BEM-treated cotton, the contact angles decreased by about 11–46° when measured at 15 s. This was due to the reduction in the amount of vinyl groups of VTES after its polymerization reaction with BEM. However, the water droplet disappeared before 25 s, and this indicated that the VTES/BEM-treated fabric was much more hydrophilic than the VTES-treated fabric because of the hydroxyl groups of BEM.

Morphology of the treated cotton surface by SEM

The SEM micrograph in Figure 6(a) shows the clean surface of the untreated cotton fiber. Figure 6(b) shows that there was no dramatic change in the surface morphology after the VTES treatment. To investigate the role of the silane coupling agent, the untreated cotton was coated by BEM with and without the silane pretreatment. Figure 6(c) shows the cotton surface treated by 2.0 mM BEM without the silane treatment. Without the silane treatment, the poly(BEM) coated on the fiber surface was not uniform. On the other hand, VTES/BEM-treated cotton, shown in Figure 6(d), had a more uniform coating of poly(BEM) on the fiber surface with no polymer deposition in the spaces between the fibers.

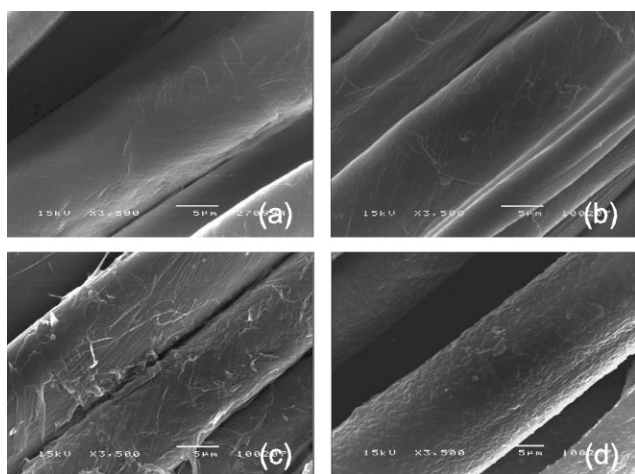


Figure 6 SEM micrographs of (a) untreated cotton, (b) 5 vol % VTES-treated cotton, (c) 2.0 mM BEM-treated cotton without silane pretreatment, and (d) 5% vol VTES/2.0 mM BEM-treated cotton.

UV absorption spectra of the VTES/BEM-treated fabric

The UV absorption of BEM is shown in Figure 7. With absorption peaks at 240, 300, and 340 nm, the spectrum shows that BEM strongly absorbs UV radiation. There is no absorption in the visible range (400–700 nm), and this means that the presence of BEM on the fabric would show no color. The UV transmission spectra of untreated cotton and cotton treated with 5 vol % VTES and 1.0, 2.0, or 10.0 mM BEM are shown in Figure 8. The transmission of the cotton treated with 10.0 mM BEM was almost cut off in the UVB region (280–315 nm) and was up to 370 nm in the UVA region. In the spectra for low concentrations of BEM, some transmission around 260 nm can be observed. This corresponds to the wavelength of minimum absorption of BEM, as shown in Figure 7. These characteristic UV absorption spectra

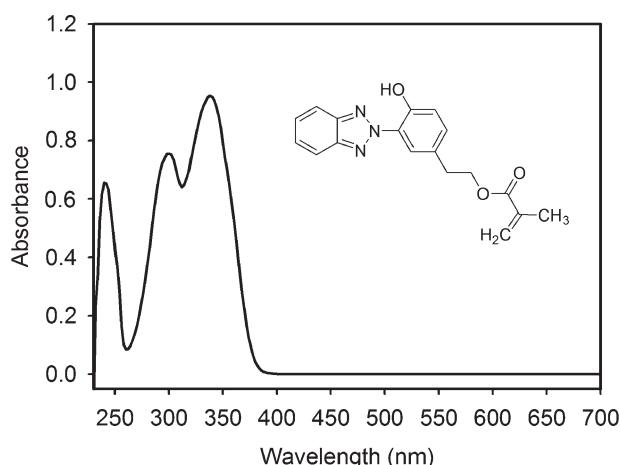


Figure 7 UV spectrum of BEM.

of the treated fabrics indicate that the reduction of UV transmission in the treated fabrics was due to the UV absorption of BEM coated on the fabric surface.

UPF of the treated fabric

UPF is defined as the ratio of the average effective UV irradiance calculated for unprotected skin to the average effective UV irradiance calculated for skin protected by the test fabric. UPF can be calculated as follows²⁰:

$$UPF = \frac{\sum_{280\text{nm}}^{400\text{nm}} E_{\lambda} S_{\lambda} \Delta\lambda}{\sum_{280\text{nm}}^{400\text{nm}} E_{\lambda} S_{\lambda} T_{\lambda} \Delta\lambda} \quad (1)$$

where E_{λ} is the relative erythemal spectral effectiveness, S_{λ} is the solar spectral irradiance ($\text{W m}^{-2} \text{nm}^{-1}$), T_{λ} is the average spectral transmittance of fabric, and $\Delta\lambda$ is the measured wavelength interval (nm).

The calculated UPF value indicates how much longer a person can stay in the sun when fabric covers the skin versus the length of time he can stay in the sun without a fabric covering and obtain the same erythemal response.²⁰ According to AS/NZ 4399 : 1996,²³ the UV-protection level of fabrics can be rated according to their UPF values into three levels: good (UPF = 15–24), very good (UPF = 25–39), and excellent (UPF \geq 40).

In this work, the untreated cotton was found to have a very low UPF of only 4, and this value remained relatively unchanged after the silane treatment. This indicates that the silane treatment did not affect the UV-protection properties of the fabric. The poly(BEM)-coated fabric using 2.0 mM BEM without the silane pretreatment showed a significant

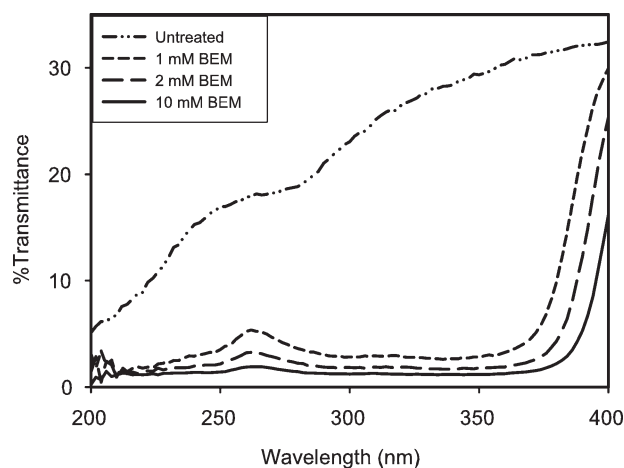


Figure 8 UV spectra of untreated cotton and cotton treated with 5 vol % VTES and then polymerized with BEM at the concentrations of 1.0, 2.0, and 10 mM with a DMAC/water ratio of 1 : 1.

increase in the UPF value from 4 to 37, whereas the sample with 5% VTES pretreatment had excellent UV protection with a high UPF value of 54. The results show that VTES played a very important role in improving the UV-protection property of the fabric by providing vinyl groups on the cotton surface to polymerize with BEM, resulting in a uniform film of a poly(BEM) coating on the fiber surface.

Effect of DMAC on the polymerization of BEM

In the polymerization step, DMAC was used to dissolve BEM. To make the coating method environmentally friendly, the optimum ratio of the organic solvent to water in the system was determined. Figure 9 presents SEM micrographs of 5 vol % VTES/2.0 mM BEM-treated cotton with different amounts of DMAC in water. It was found that the surface morphology of the coating was affected by the amount of DMAC added. With low amounts of DMAC, the polymer coating was not uniform. This was due to the low solubility of BEM in water. Large particles of the polymer were seen on the fiber surface and in the spaces between the fibers. The presence of the polymer particles between the fibers led to the very high UPF value of 80, as shown in Figure 10. When the ratio of DMAC to water increased to 1 : 1, the UPF value of the treated fabric was found to decrease, but it was still as high as 54. From the SEM micrograph in Figure 9(c), it can be seen that a uniform coating was obtained in this case with no polymer deposition in the spaces between the fibers. This therefore led to a reduction in UPF of the treated fabric in comparison with the previous two samples. However, when the amount of DMAC was too high, the good solubility of BEM made the polymerization of BEM occur mostly in

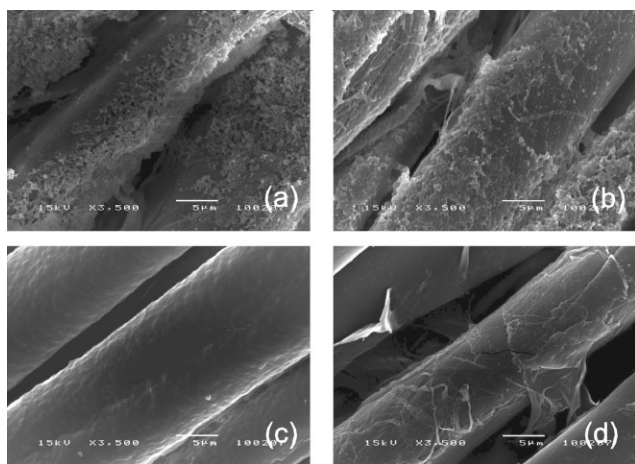


Figure 9 SEM micrographs of 5 vol % VTES/2.0 mM BEM-treated cotton with (a) 5, (b) 10, (c) 17.5, and (d) 25 mL of DMAC in a total volume of 35 mL.

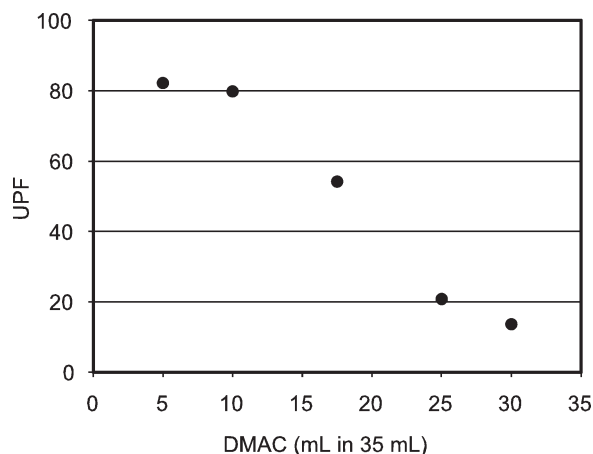


Figure 10 Effect of the amount of DMAC used in the polymerization process on the UPF of cotton fabrics treated with 5 vol % VTES and 2.0 mM BEM.

the solution with a nonuniform coating on the fiber surface. In this case, the UPF value of the treated fabric also decreased to a value of 21 or even lower. Thus, the ratio of DMAC to water of 1 : 1 was found to be the optimum ratio for the treatment.

Effect of the VTES concentration

The effect of the VTES concentration used in the silane treatment was investigated. Figure 11 shows SEM micrographs of 2 mM BEM-treated cotton pretreated with different silane concentrations. The VTES concentration of 1 vol % seemed not to be enough to provide a uniform coating. A uniform coating was obtained with VTES concentrations of 5, 10, and 15 vol %. However, the polymer film became rougher when the concentration of VTES increased. This may be due to the increase in the number of

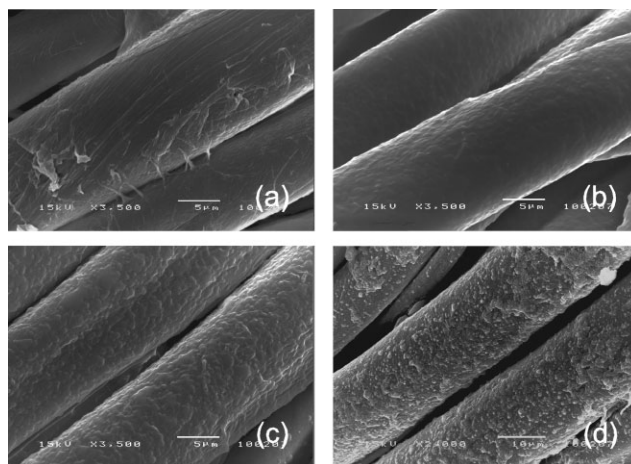


Figure 11 SEM micrographs of 2 mM BEM-treated cotton pretreated with different silane concentrations: (a) 1, (b) 5, (c) 10, and (d) 15 vol %.

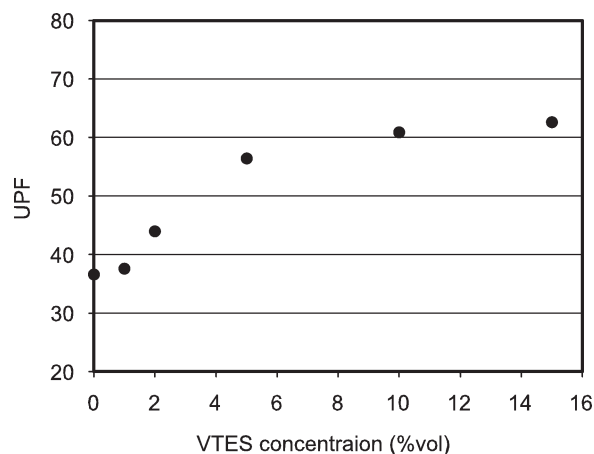


Figure 12 Effect of the VTES concentration on the UPF of cotton fabrics treated with 2.0 mM BEM.

initiation sites on the silane-treated fabric. Besides, with more vinyl groups on the fiber surface, more polymer was attached to the surface. The UPF values therefore increased with increasing VTES concentration, as shown in Figure 12. This result indirectly indicates that the vinyl groups of silane reacted with BEM during polymerization; otherwise, the UPF values should have remained constant with the same amount of BEM when the VTES concentration increased. However, the UPF values increased slightly and tended to level off when the VTES concentration further increased, and this indicated that the surface coverage of vinyl groups was near saturation and the excess silane molecules were not involved in the polymerization with BEM. It is interesting to note also that the UV-protective capability of the fabric treated with 2.0 mM BEM could be raised from very good (UPF < 40) to excellent (UPF > 40) with the use of the VTES pretreatment.

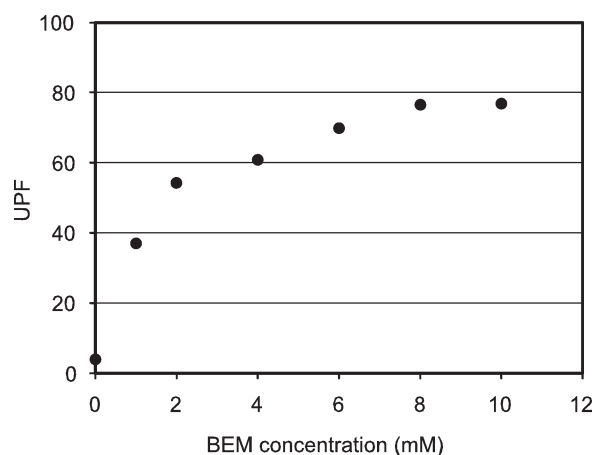


Figure 13 Effect of the BEM concentration on the UPF of cotton fabrics treated with 5 vol % VTES.

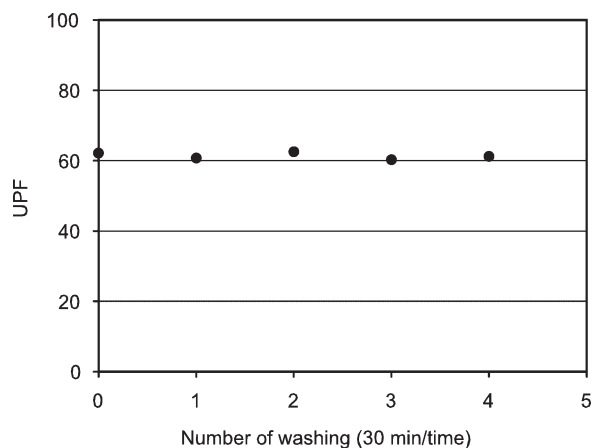


Figure 14 UPF of 5 vol % VTES/4.0 mM BEM-treated cotton after washing at 90°C and 30 rpm for 30 min per time.

Effect of the BEM concentration on the UV-protection properties of the treated fabric

The effect of the BEM concentration on the UV-protection properties of the treated fabric was studied. The results are reported in Figure 13, which indicates that a higher BEM concentration resulted in a higher UPF value. From Figure 13, it can be concluded that the cotton fabric, which had a UPF of 4 before treatment, can provide excellent UV protection with a UPF value of more than 40 after polymerization using BEM with a concentration of 2.0 mM, and the maximum UPF value of over 77 was obtained with a BEM concentration of 10.0 mM. A further increase in the BEM concentration did not lead to a further increase in UPF. This may be due to the limited amount of VTES on the fabric.

Durability of the treated surface

Figure 14 shows the UPF values of the 5 vol % VTES/4.0 mM BEM-treated cotton at different washing times. The UPF value of the fabric remained almost unchanged even after washing at 90°C 4 times at 30 min per time. Similar results were obtained with fabrics treated with different amounts of VTES and BEM. Thus, with this coating method, the coated fabrics showed excellent washing resistance at 90°C. This was due to the direct chemical bonding between the silane and substrate²⁴ and the covalent bond formation between the vinylsilane and polymer.²⁵

CONCLUSIONS

UV-protective cotton fabric can be produced by the polymerization of BEM on VTES-treated fabrics. VTES plays an important role by providing vinyl groups to the cotton surface to polymerize with

BEM, resulting in a more uniform coating and a fabric with a higher UPF than that of a fabric coated without the VTES pretreatment. With a 5 vol % VTES pretreatment and a BEM concentration greater than 2.0 mM, cotton fabric with a low UPF of 4 before treatment provided excellent UV protection after the polymerization, and the protection remained almost unchanged even after four washes at 90°C for 30 min per time.

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