

CHAPTER VII
GRAFTING POLYMERIZATION OF
2-[3-(2H-BENZOTRIAZOL-2-YL)-4-HYDROXYPHENYL]ETHYL
METHACRYLATE ON VINYLTRIETHOXYSILANE-TREATED COTTON
FOR PREPARATION OF UV-PROTECTIVE FABRICS*

7.1 Abstract

Vinyltriethoxysilane was used to modify cotton surface to provide polymerizable vinyl groups on the fiber surface. The UV-absorbing monomer, 2-[3-(2H-benzotriazol-2-yl)-4-hydroxyphenyl]ethyl methacrylate (BEM), was polymerized on the vinyltriethoxysilane-treated fabric in order to prepare UV-protective cotton. The effects of the amounts of solvent, silane coupling agent, and BEM, on surface morphology and Ultraviolet Protection Factor (UPF) of the treated cotton fabric were investigated. With a suitable process, poly(BEM) was successfully coated on the fabric and it significantly reduced ultraviolet transmission through the fabric resulting in a cotton fabric with excellent UV-protection property. The use of silane coupling agent helped to ensure a polymer coating with good uniformity and good resistance to washing.

Key words: Surface grafting; Silane; Polymerization; UV-protective cotton fabric

7.2 Introduction

Silane coupling agents have been widely employed for surface modifications. They are often used to improve the adhesion between a polymer matrix and

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reinforcements.¹ The general formula of organosilanes is $\text{RSi}(\text{OR}')_3$ where R and R' represent an organofunctional and a hydrolysable groups, respectively. Vinyltriethoxysilane (VTES), which is relatively inexpensive, has been used to modify glass surface to improve its scratch protection,² 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, which 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 on the use of this technique to modify a textile fabric.

The UV-protective properties of clothing have received much attention in recent years due to the hazardous effects UV radiation on human skin. The factors affecting the extent of protection rendered by clothing have been reported.⁹⁻¹² The change in sun exposure habits over the past few decades and the increase in incidences of skin cancer are some of the reasons that have made UV-protective property of fabrics 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 in the dyeing process,¹³⁻¹⁴ and the synthesis of dyes with UV-absorber.¹⁵ In the present study an organic monomer containing a UV-absorbing system was applied on to cotton which was pretreated by VTES via graft polymerization. The monomer, 2-[3-(2H-benzotriazol-2-yl)-4-hydroxyphenyl]ethyl methacrylate (BEM), was used in this study due to the strong photostability of benzotriazole.¹⁶ Benzotriazole, with intramolecular hydrogen bond in its structure, strongly absorbs UV radiation and rapidly dissipate the energy through a mechanism which 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 the present study are depicted in the schematic shown in Figure 7.1. In the reaction VTES reacted at the hydrolyzed silicon orthoester functionality with cotton and at the vinyl group with the monomer containing a UV-absorbing system. The ethoxy groups in VTES were first hydrolyzed to silanol groups which then formed hydrogen bonding 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 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 by scanning electron microscopy (SEM) and Fourier transform infrared attenuated reflection spectroscopy (FTIR-ATR).

7.3 Experimental

7.3.1 Materials

A plain weave, medium-weight (150 g/m²), cotton fabric was purchased from Boonchaury Co. Ltd. The fabric was desized, scoured, and bleached at the factory. Prior to 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 Company (USA). Ammonium persulfate (99%) was purchased from Asia Pacific Specialty Chemicals Ltd (Australia). Dimethylacetamide (DMAC) (99.5%) was purchased from Labscan Company (Ireland). All chemicals were used without further purification.

7.3.2 Modification of Cotton Fabric by VTES-BEM

VTES was hydrolyzed in aqueous solution in the concentration range of 1 – 15 %vol. The pH of the silane aqueous solution was adjusted to 4 by using 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 solution was 1:20. The fabrics obtained were dried in an oven for 5 h at 120°C in order 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 the temperature of 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 in order to 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 dry. After that it was washed with water and dried once again.

7.3.3 Characterization of the Treated Cotton Surface

Scanning electron microscopy (JEOL, JSM 5200, 15 kv) was used to study surface morphology of the coated fabric. Fourier transform infrared attenuated reflection spectroscopy with a ZnSe plate was used to analyze the chemical groups present on the cotton surface. The spectrometer used was Nexus 670 spectrometer (Nicolet) with 32 scans at a 4 cm⁻¹ resolution in the frequency range of 4000-400 cm⁻¹. The water contact angles of the treated surface were measured using a KRÜSS contact angle measurement instrument, DSA 10-Mk2. A water droplet with the volume of 10 µL was placed onto the tested surface and the dynamic contact angles of the droplet were measured after 15 and 25 s.

7.3.4 Determination of the UV Protection Property of the Treated Fabric

Determination of the UV protection property of the treated fabric was based on the AATCC Test Method 183-2004.¹⁷ The UV transmission of the fabric was measured using Shimadzu UV spectrophotometer 2550 with integrating sphere attachment ISR-2200. The percent transmittance for wavelengths from 280 to 400 nm was measured in intervals of 2 nm. Three measurements of the UV transmittance were performed for each specimen, in warp, weft, and diagonal directions. The results are the mean values of the three measurements from duplicate specimens. The data are then used to calculate the Ultraviolet Protection Factor (UPF) of the fabric.

The durability of the UV protection property of the treated fabric was determined by the washing fastness tests. The washing was carried out in water in the dyeing machine DAELIM DL-6000 at 30 °C with the speed of 30 rpm and 30 min/time. The fabric to water ratio was 1:100.

7.4 Results and Discussion

7.4.1 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 7.2. 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 =CH₂. The peak at 1274 cm^{-1} is due to CH=CH₂ in-plane bending.¹⁸ When the amount of VTES used in silane treatment increased, the characteristic peaks of the vinyl groups appeared with higher intensity, thus confirming that VTES has been successfully attached to the fabric 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 7.3 compares the FTIR-ATR spectra of the untreated cotton, 5 %vol VTES-treated, and 5 %vol VTES/6.0 mM BEM-treated cotton. From the spectra, the additional peaks of BEM can be seen at 1517 cm^{-1} assigned to C=C of substituted benzene ring and 1730 cm^{-1} assigned to C=O stretching. In addition, there were peaks at 1250 and 1150 cm^{-1} due to C-O stretching of ester, and the peak at 745 cm^{-1} due to C-H out-of-plane bending of the benzene ring of benzotriazole.¹⁸ The observed characteristic peaks of poly(BEM) confirmed that poly(BEM) was successfully coated on the cotton surface.

7.4.2 Characterization of the Treated Fabric Surface by Contact Angle

Measurements

The existence of vinyl groups on the cotton surface can be observed indirectly by water contact angle measurements. Normally a water droplet will disappear immediately on untreated cotton due to the hydrophilicity of its hydroxyl groups. Table 7.1 shows the contact angles of VTES-treated and VTES/BEM-treated cotton as measured by the sessile drop method. It can be seen that the contact angles of VTES-treated cotton after 25 s were in the range 134.9 - 150.5° which are much higher than 90° , and the higher the amount of VTES used, the higher the contact angle. The results thus showed that the presence of vinyl groups changed the cotton surface from a hydrophilic to a hydrophobic surface. This is clearly confirmed by Figure 7.4 which shows a water droplet on the VTES-treated cotton surface still retaining its near spherical shape even after 25 s.

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

7.4.3 The Morphology of the Treated Cotton Surface by SEM

SEM micrograph in Figure 7.5 (a) shows the clean surface of the untreated cotton fiber. Figure 7.5 (b) shows that there was no dramatic change in the surface morphology after the VTES treatment. In order to investigate the role of silane coupling agent, the untreated cotton was coated by BEM with and without the silane pretreatment. Figure 7.5 (c) shows the cotton surface treated by 2.0 mM BEM without the silane treatment. It can be seen that, without the silane treatment, the poly(BEM) coated on the fiber surface was not uniform. On the other hand, a VTES/BEM treated cotton, shown in Figure 7.5 (d), had a more uniform coating of poly(BEM) on the fiber surface with no polymer deposition in the spaces between the fibers.

7.4.4 The UV Absorption Spectra of VTES/BEM-Treated Fabric

The UV absorption of BEM is shown in Figure 7.6. The spectrum shows that BEM strongly absorbs UV radiation with absorption peaks at 240, 300 and 340 nm. There is no absorption in the visible range (400-700 nm) which means that the presence of BEM on the fabric would show no color. The UV transmission spectra of untreated cotton and treated cotton using 5 %vol VTES and 1.0, 2.0, and 10.0 mM of BEM are shown in Figure 7.7. The transmission of the treated cotton using 10.0 mM of BEM was almost cut off in UV-B region (280-315 nm) and up to 370 nm in UV-A region. In the spectra at 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 7.6. These characteristic UV absorption spectra of the treated fabrics indicate that the reduction in UV transmission of the treated fabrics was due to the UV absorption of BEM coated on the fabric surface.

7.4.5 The Ultraviolet Protection Factor (UPF) of the Treated Fabric

The Ultraviolet Protection Factor (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 follows¹⁷:

$$UPF = \frac{\sum_{280nm}^{400nm} E_{\lambda} S_{\lambda} \Delta\lambda}{\sum_{280nm}^{400nm} E_{\lambda} S_{\lambda} T_{\lambda} \Delta\lambda} \quad (7.1)$$

where:

E_{λ} = relative erythemal spectral effectiveness

S_{λ} = solar spectral irradiance in $Wm^{-2}nm^{-1}$

T_{λ} = average spectral transmittance of fabric

$\Delta\lambda$ = measured wavelength interval in nm

The calculated UPF value indicates how much longer a person can stay in the sun when fabric covers the skin, as compared with the length of time in the sun without fabric covering to obtain the same erythemal response.¹⁷ According to AS/NZS 4399: 1996,¹⁹ 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 increase in UPF value from 4 to 37, while the sample with 5 %-VTES pretreatment had an 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 the vinyl groups on the cotton surface to polymerize with BEM resulting in a uniform film of poly(BEM) coating on the fiber surface.

7.4.6 The Effect of DMAC on the Polymerization of BEM

In the polymerization step, DMAC was used to dissolve BEM. In order to make the coating method environmental friendly, the optimum ratio of organic solvent to water used in the system was determined. Figure 7.8 represents the SEM micrographs of 5 %vol VTES/2.0 mM BEM-treated cotton using different amounts of DMAC in water. It was found that the surface morphology of the coating was affected by the amount of DMAC added. At low amounts of DMAC, the polymer coated was not uniform. This is 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 in between the fibers led to the very high UPF values of 80 as shown in Figure 7.9. When the ratio of DMAC: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 7.8 (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 has therefore led to a reduction in UPF of the treated fabric when compared to the previous two samples. However, when the amount of DMAC was too high, the good solubility of BEM made the polymerization of BEM occurred mostly in the solution with 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:water of 1:1 was found to be the optimum ratio for the treatment.

7.4.7 The Effect of the VTES Concentration

The effect of VTES concentration used in the silane treatment was investigated. Figure 7.10 shows the SEM micrographs of 2 mM BEM-treated cotton pretreated by different silane concentrations. The VTES of 1 %vol seemed not to be enough to give a uniform coating. The uniform coating was obtained by using VTES 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 initiation sites on the silane-treated fabric. Besides, the more vinyl groups present on the fiber surface, the more polymer attaching to the surface. The UPF values therefore increased with increasing

VTES concentration as shown in Figure 7.11. This result indirectly indicated that the vinyl groups of silane reacted with BEM during polymerization, otherwise the UPF values should remain constant at the same amount of BEM when VTES concentrations increased. However, the UPF values increased slightly and tended to level off when VTES concentration further increased, indicating that the surface coverage of vinyl groups was near saturation and the excess silane molecules did not involve in the polymerization with BEM.

7.4.8 The Effect of BEM Concentration on the UV-Protection Property of the Treated Fabric

The effect of BEM concentration on the UV protection property of the treated fabric was studied. The results are reported in Figure 7.12, which indicates that higher BEM concentration resulted in higher UPF. From Figure 7.12, it can be concluded that the cotton fabric, which has 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. Further increase in BEM concentration did not lead to further increase in UPF. This may be due to the limited amount of VTES on the fabric.

7.4.9 The Washing Fastness of the Treated Fabric

Figure 7.13 shows the UPF values of the 5 %vol VTES/4.0 mM BEM-treated cotton at different times of washing. It can be seen that UPF of the fabric was almost unchanged even after 10 times of washing at 30 °C. Thus, with this coating method, the coated fabric shows excellent washing resistance at 30 °C. This is due to the direct chemical bonding between silane and substrate,²⁰ and the covalent bond formation between vinylsilane and polymer.²¹

7.5 Conclusions

The UV-protective cotton fabric can be produced by polymerization of 2-[3-(2H-benzotriazol-2-yl)-4-hydroxyphenyl]ethyl methacrylate (BEM) on vinyltriethoxysilane-treated fabrics. VTES plays an important role of providing vinyl groups on cotton surface to polymerize with BEM resulting in a more uniform coating and a fabric with a higher UPF than that of the fabric coated without VTES pretreatment. With a 5 %vol VTES pretreatment and a BEM concentration greater than 2.0 mM, the cotton fabric, which has a low UPF of 4 before treatment, could provide excellent UV protection after the polymerization and the protection remained almost unchanged even after 10 times of washing.

7.6 Acknowledgment

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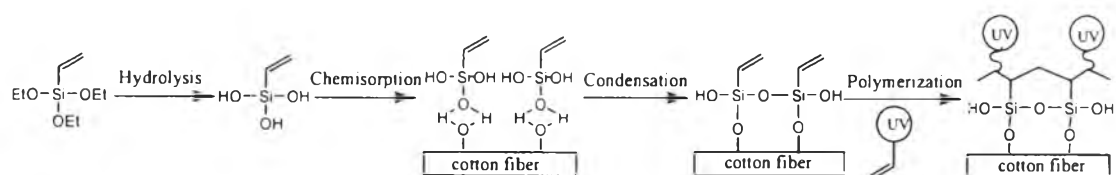


Figure 7.1 The reaction scheme of grafting polymerization.

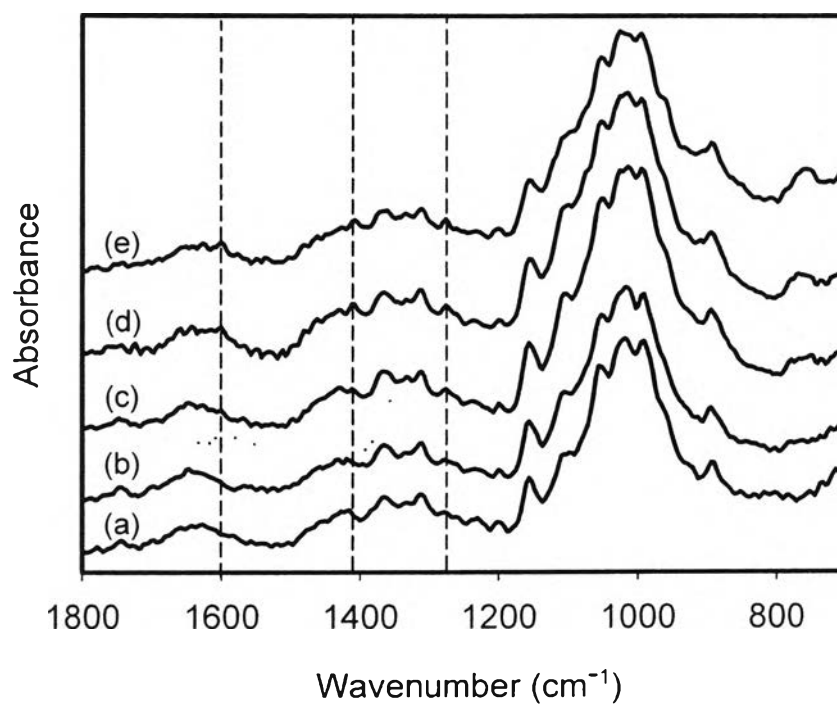


Figure 7.2 The FTIR-ATR spectra of (a) untreated cotton, and silane-treated cotton using (b) 1 %vol, (c) 5 %vol, (d)10 %vol, and (e)15 %vol.

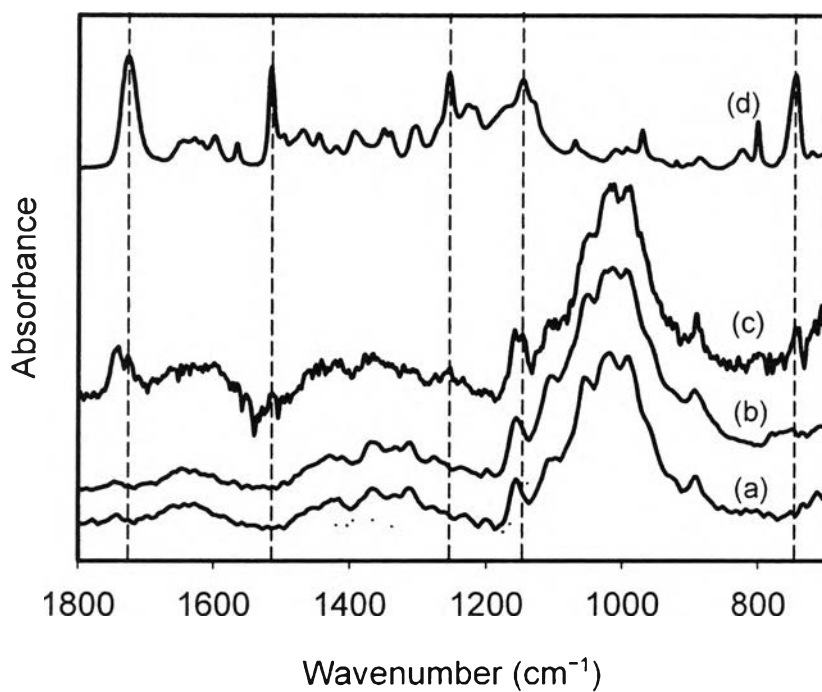


Figure 7.3 The FTIR spectra of (a) untreated cotton, (b) 5 %vol VTES-treated cotton, (c) 5 %vol VTES/6.0 mM BEM-treated cotton, and (d) poly(BEM).

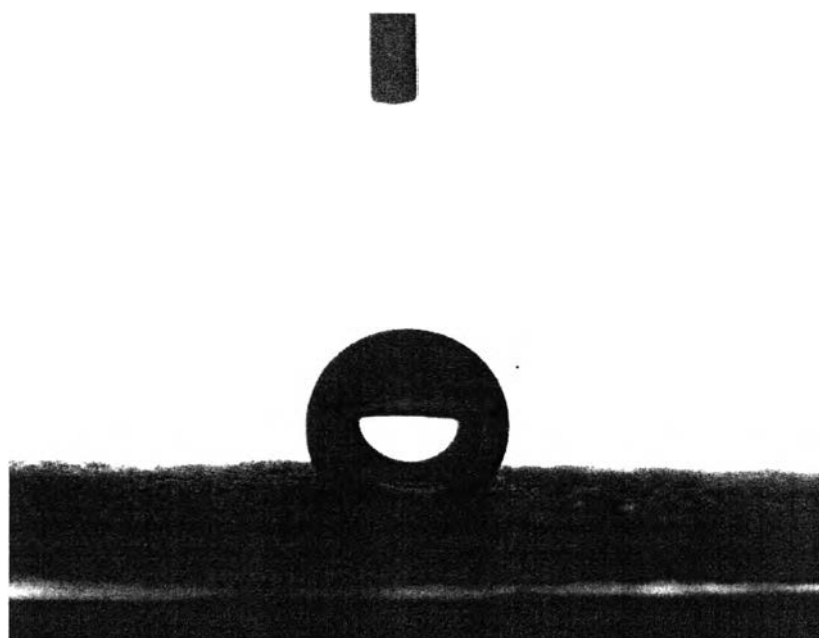


Figure 7.4 The water droplet on 15 %vol VTES-treated cotton at 25 s.

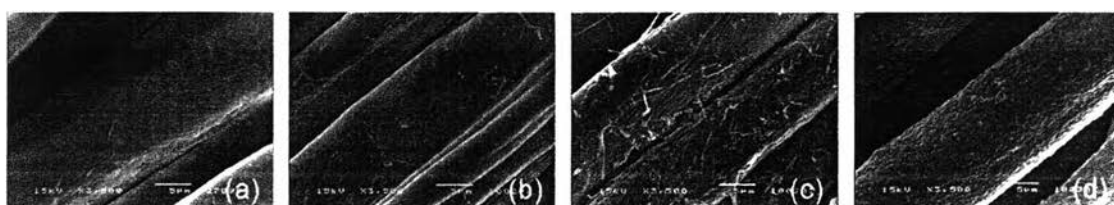


Figure 7.5 SEM micrographs of (a) untreated cotton, (b) 5 %vol VTES-treated cotton, (c) 2.0 mM BEM-treated cotton without silane pretreatment, and (d) 5 % vol VTES/2.0 mM BEM-treated cotton.

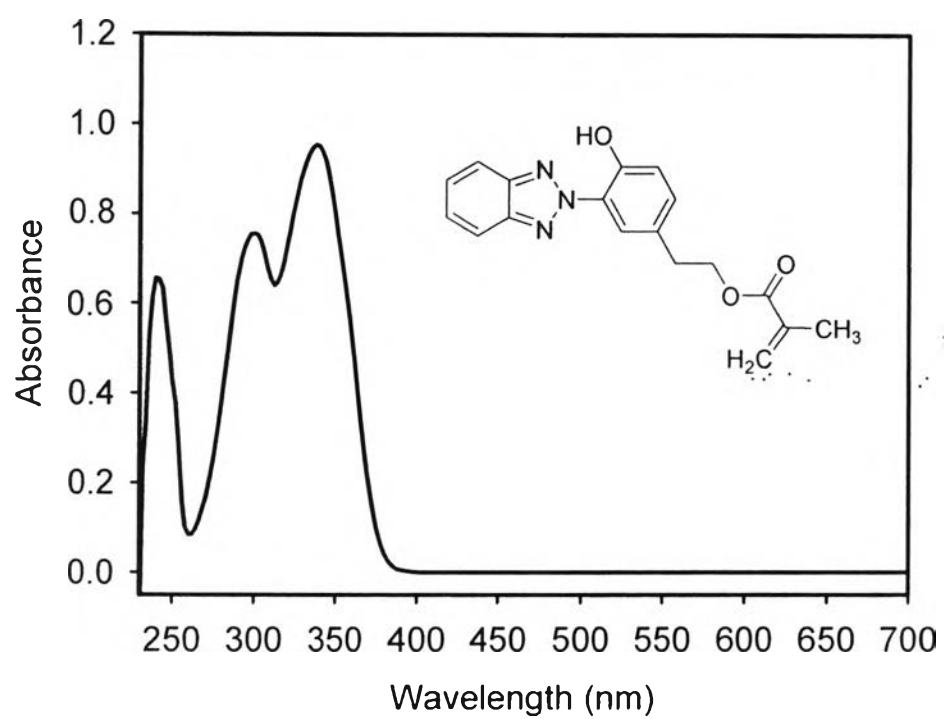


Figure 7.6 UV spectrum of 2-[3-(2H-benzotriazol-2-yl)-4-hydroxyphenyl]ethyl methacrylate (BEM).

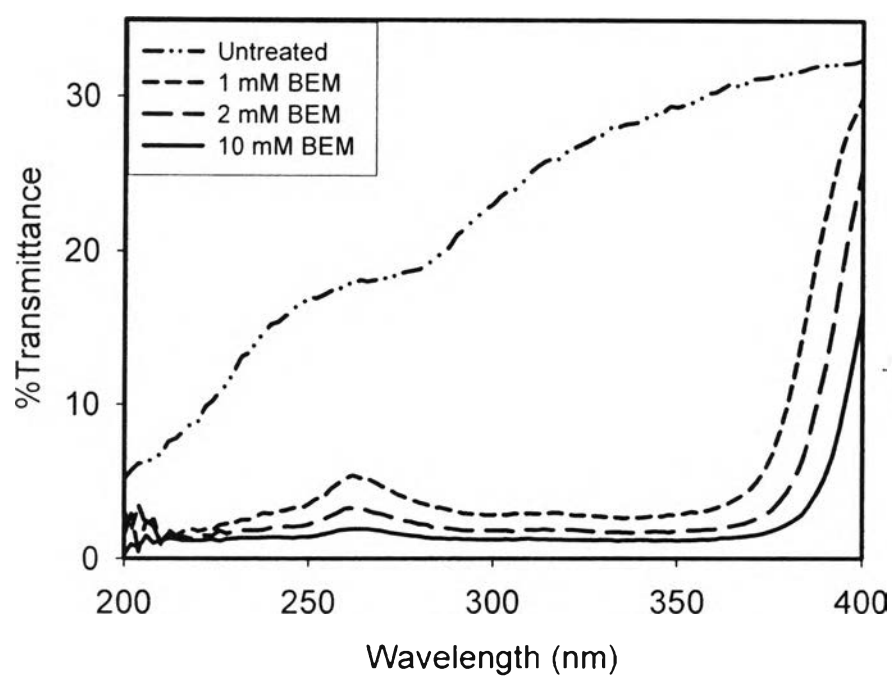


Figure 7.7 The UV spectra of untreated cotton, and treated cotton using 5 %vol VTES followed by polymerization with BEM at the concentrations of 1.0, 2.0, and 10 mM, using a DMAC:water ratio of 1:1.

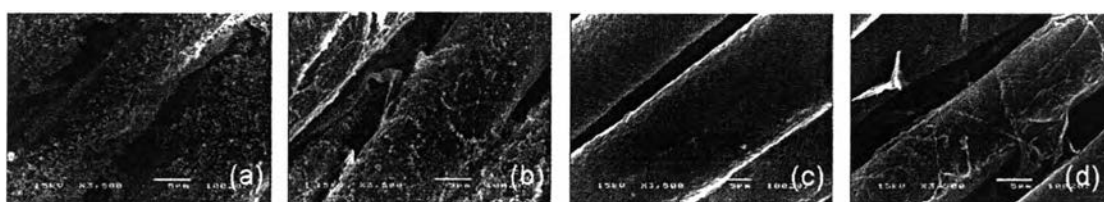


Figure 7.8 SEM micrographs of 5 %vol VTES/2.0 mM BEM-treated cotton using (a) 5mL, (b) 10 mL, (c) 17.5, and (d) 25 mL, of DMAC in the total volume of 35 mL.

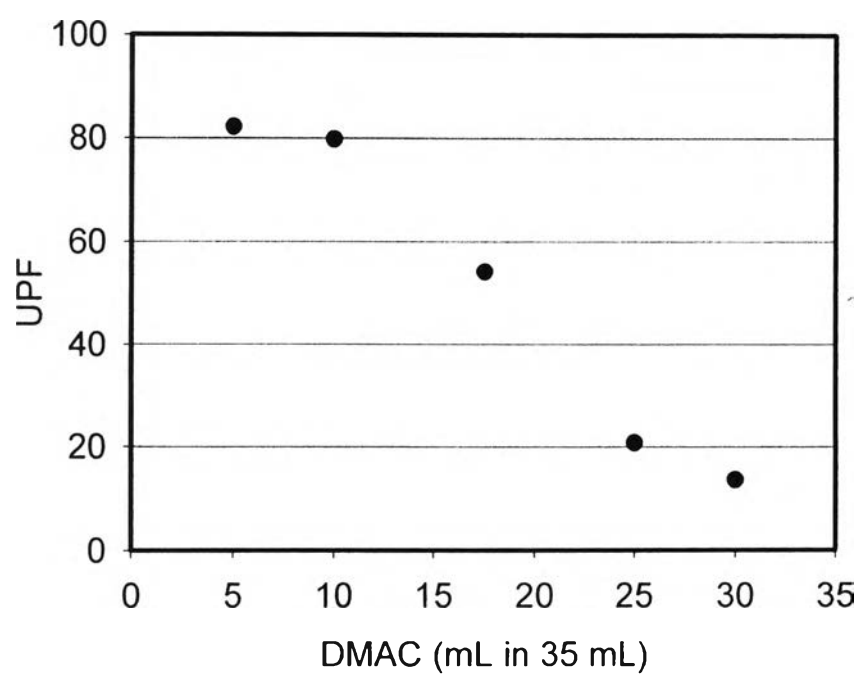


Figure 7.9 The effect of the amount of DMAC used in the polymerization process on the UPF of treated cotton fabrics using 5 %vol VTES and 2.0 mM BEM.

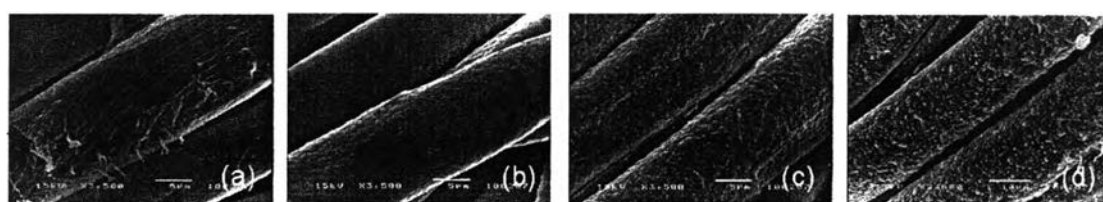


Figure 7.10 SEM micrographs of 2 mM BEM-treated cotton pretreated by different silane concentrations; (a) 1 %vol, (b) 5 %vol, (c) 10 %vol, and (d) 15 %vol.

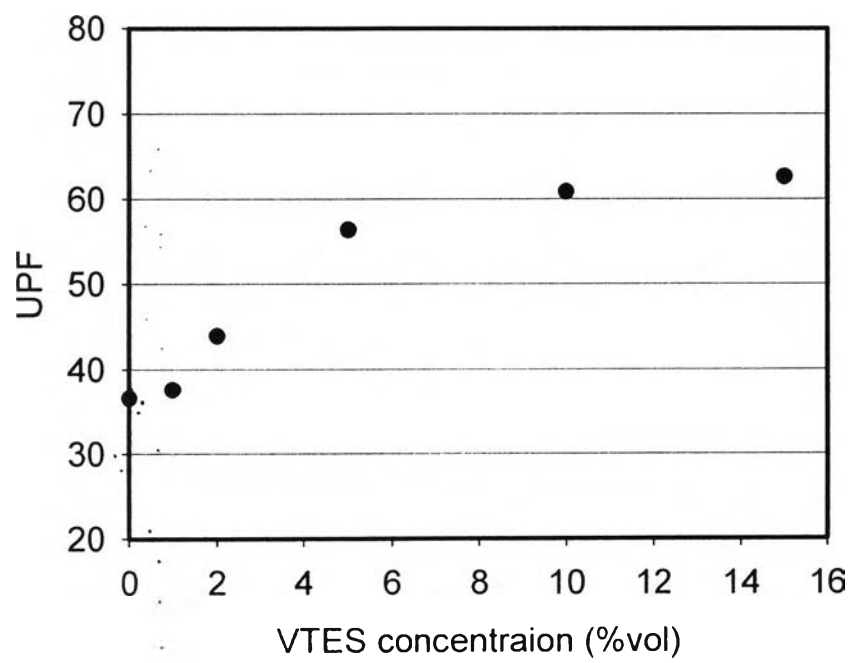


Figure 7.11 The effect of VTES concentration on the UPF of treated cotton fabrics using 2.0 mM BEM.

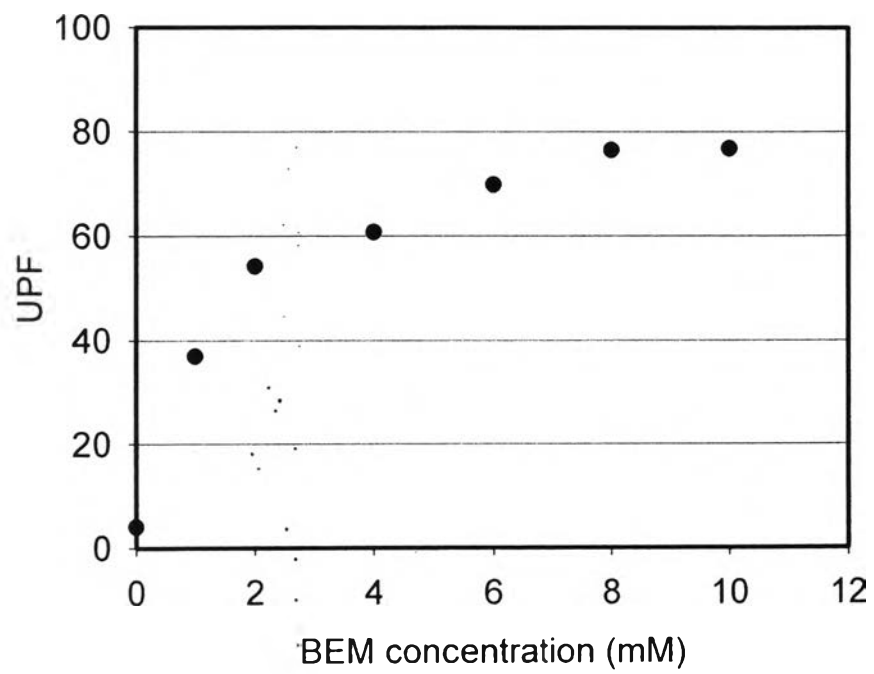


Figure 7.12 The effect of BEM concentration on the UPF of treated cotton fabrics using 5 %vol VTES.

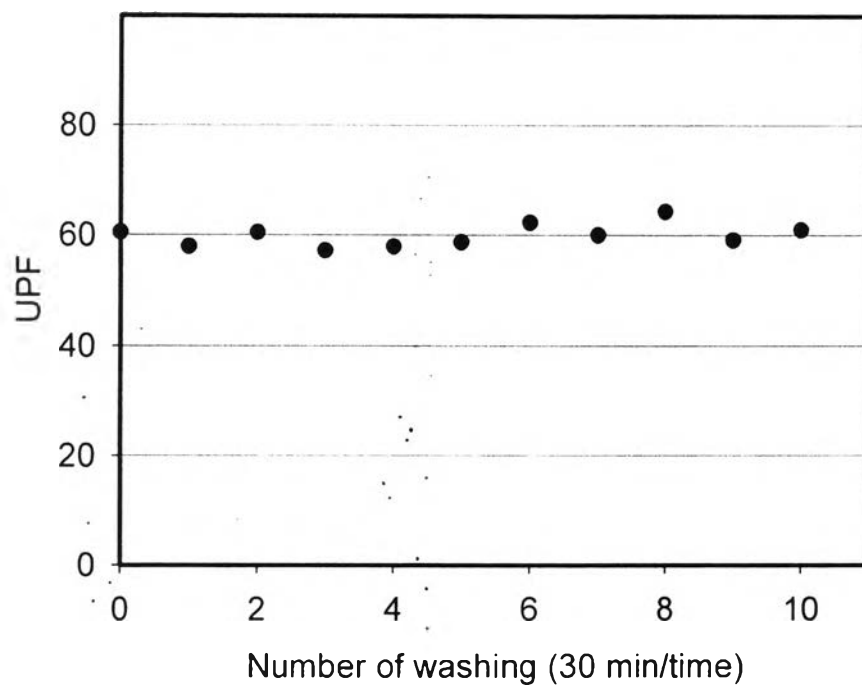


Figure 7.13 The washing fastness of 5 %vol VTES/4.0 mM BEM-treated cotton at 30 °C, 30 rpm and 30 min/time.

Table 7.1 Water contact angle of VTES-treat 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.