Article

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Enhancement of Antibacterial Capability of Cotton Textiles Coated with TiO_2–SiO_2/Chitosan Using Hydrophobization

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Since textiles have a porous and hydrophilic structure, they are ideal substrates for the settlement and growth of pathogenic bacteria. Therefore, fabrication of hydrophobic textiles to reduce their humidity has the potential to inhibit the growth of bacteria. On this basis, we report here an improvement of the antibacterial capability of textiles coated with TiO_2–SiO_2/chitosan using hydrophobization. Synthesis of TiO_2–SiO_2 clusters with chitosan was carried out using the sol–gel technique. In addition, hydrophobization of the textiles using hexadecyltrimethoxysilane (HDTMS) was carried out using a dip-spin coating method. In addition, their characteristics were examined using X-ray diffraction (XRD), scanning electron microscopy (SEM), UV–vis diffuse reflectance spectra (UV-DRS), Fourier transform infrared (FTIR), water contact angle, and antibacterial activity. XRD, SEM, UV-DRS, FTIR, and water contact angle confirmed the physical and chemical properties of the modified textiles. In summary, the present work shows that the hydrophobization of textiles using HDTMS can enhance the antibacterial capability of cotton textiles.

Keywords: Titanium dioxide; Silicon dioxide; Hexadecyltrimethoxysilane; Hydrophobization.

INTRODUCTION

Modification of textiles to enhance their physical, chemical, and biological properties is becoming increasingly desirable for several applications.[1–7] Textiles with enhanced resistance against microorganisms (e.g., antibacterial and antimicrobial textiles) have been widely investigated in recent years since they are utilized for various applications such as in medical devices, health care, hygiene, water purification systems, hospitals, and dental surgery equipment.[8] Therefore, several methods to improve the antibacterial capability of textiles have been proposed and are still being devised.[8–13]

Preparation of antibacterial textiles can be achieved by designing them with a simple technique using metal nanoparticles with sizes ranging from 1 to 100 nm.[14–20] Various approaches have been proposed to modify textiles with nanomaterials, such as sol–gel technique, magnetron sputter-coating, plasma deposition, and layer-by-layer formation. Among these, the sol–gel method is the most popular one because of its comparative ease of preparation. The use of several nanomaterials such as titanium dioxide (TiO_2) and copper (Cu) has been established.[21,22] TiO_2 is widely explored because of its remarkable physical, chemical, and biological properties compared to Cu.

Textiles have a porous and hydrophilic structure, so they are an ideal base for the settlement and growth of pathogenic bacteria.[21] Therefore, the fabrication of hydrophobic or superhydrophobic textiles seems a good strategy to enhance their antibacterial capability. Hydrophobic textiles can be defined as those with water repellency with a water contact angle (WCA) ≥ 90°.

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Contrarily, if the WCA is <90°, the textile can be classified as hydrophilic.

Therefore, this work aims to investigate the enhancement of the antibacterial capability of the textiles via hydrophobization using hexadecyltrimethoxysilane (HDTMS). It is highly beneficial to provide a suitable technique to produce antibacterial textiles for future medical applications. Since chitosan and TiO_2 are also well known to have antibacterial properties, the use of these materials is expected to further improve the antibacterial capability of textiles. Also, hydrophobization was carried out to produce hydrophobic textiles. It is well established that hydrophobic textiles are more effective in removing impurities and reducing humidity so that these materials have the potential to inhibit the growth of bacteria.

The rest of this paper is organized as follows. Materials used in this work are first presented. Then, preparation of textiles by coating TiO_2–SiO_2/chitosan is described. Hydrophobization, characterization, and antibacterial investigation are then presented. The results of the work are then summarized, followed by conclusions.

EXPERIMENTAL

Materials

In this study, silk cotton cloth, titanium isopropoxide (TIP) ($C_{12}H_{28}O_4Ti$, Sigma-Aldrich, St. Louis, MO, USA), tetraethyl orthosilicate (TEOS) ($C_8H_{20}O_4Si$, Merck KGaA, Darmstadt, Germany), hydrochloric acid (HCl) (Merck KGaA, Darmstadt, Germany), acetic acid (CH_3COOH) (Merck KGaA, Darmstadt, Germany), diethanolamine (DEA) ($C_4H_{11}NO_2$, Merck KGaA, Darmstadt, Germany), isopropanol (C_3H_8O, Merck KGaA, Darmstadt, Germany), cetyl trimethyl ammonium bromide (CTAB) ($C_{16}H_{33}N$ $(CH_3)_3Br$, Merck KGaA, Darmstadt, Germany), chitosan technical ($(C_6H_{11}NO_4)n$, Merck KGaA, Darmstadt, Germany), sodium hydroxide (NaOH, Merck KGaA, Darmstadt, Germany), butane 1,2,3,4-tetra carboxylic acid (BTCA) ($C_6H_6O_8$, Sigma-Aldrich, St. Louis, MO, USA), HDTMS ($C_{19}H_{42}O_3Si$) (Sigma-Aldrich, St. Louis, MO, USA), nutrient agar (NA) medium, and cultures of *Escherichia coli*, and *Staphylococcus epidermis* were employed.

Preparation of TiO_2–SiO_2/chitosan powder

A solution containing TIP and DEA in isopropanol with the molar ratio 1:2:2 M was prepared and continuously stirred for 30 min at the room temperature. Another solution containing TEOS and hydrochloric acid in isopropanol with the molar ratio 1:0.02:2 M was also prepared under stirring for 30 min. All solutions were mixed with chitosan in acetic acid and then added with CTAB. Next, the mixture was stirred to obtain a homogeneous solution. It was then followed by dehydration at 110 °C for 15 h and calcination at 500 °C for 3 h to produce the TiO_2–SiO_2/chitosan powder.

Preparation of cotton textiles

Cotton textiles were washed using a detergent (2 g/L). Then, they were dried in an oven at 80 °C for 15 min. They were then immersed in 12 mL Na_2CO_3 (3.7×10^{-3} M) and heated at 100 °C for 5 min, washed using the distilled water, and dried at 80 °C for 15 min. This was followed by immersing them in BTCA under the room temperature for 24 h. Finally, the modified textiles were dried at 80 °C for 15 min.

Preparation of hydrophobic textiles

The coating of the cotton textiles using TiO_2–SiO_2/chitosan powder was done using the dip-spin coating method. Textiles were first immersed in an isopropanol solution containing TiO_2–SiO_2/chitosan powder and CTAB. They were then dried in an oven at 80 °C for 15 min. The coated textiles were then washed using HDTMS (0.5 mL) and then dried in an autoclave at 120 °C for 3 h.

Preparation of bacteria

Bacterial cultures were dispersed in the NA medium and incubated for 24 h. The grown bacteria were then transferred into a tube containing 10 mL of distilled water. The bacterial suspension was stored for future use.

Antibacterial appraisal

Cotton textiles coated with TiO_2–SiO_2/chitosan and textiles with nanoclusters of TiO_2–SiO_2/chitosan were cut into disks of diameter of 0.6 mm. For comparison, cotton textiles of the same size but without coating were also prepared. Next, the textiles were placed in a Petri dish containing NA that was previously

inoculated with the bacteria *S. epidermidis* and *E. coli.* The plates were then incubated for 24 h. The zone of inhibition around the cotton textiles was measured using a ruler.

Characterization

Surface morphology was studied using scanning electron microscopy (SEM, Hitachi S-3400N). X-ray diffraction (XRD) spectra were then examined using an XPERT-PRO diffractometer. Fourier transform infrared (FTIR) spectra were recorded using an XPort analytical PAN instrument. UV–vis diffuse reflectance spectra (UV-DRS) were recorded using a Shimadzu UV-450 spectrometer. The hydrophobic properties were studied using the WCA. For this examination, the textile sample was placed on a glass plate and a camera was placed 10 cm away from the sample. A drop (0.1 mL) of distilled water was placed on the samples and the WCA was measured.

RESULTS AND DISCUSSION

XRD characteristics

The XRD pattern of TiO_2–SiO_2/chitosan is shown in Figure 1. It is seen that TiO_2–SiO_2/chitosan has intensity peaks at 2θ = 25°, 38°, 48°, 53°, 55°, 62°, 68°, 70°, 75°, and 82°. From their intensities, the prominent peaks are at 2θ = 25°, 38°, and 48°. These characteristics can be identified with the anatase phase of TiO_2 with a tetragonal geometry that has *hkl* (1,0,1), (0,0,4), and (2,0,0) reflections. Moreover, by using the Scherrer's formula, the TiO_2 crystal size was estimated as 13.07 nm.

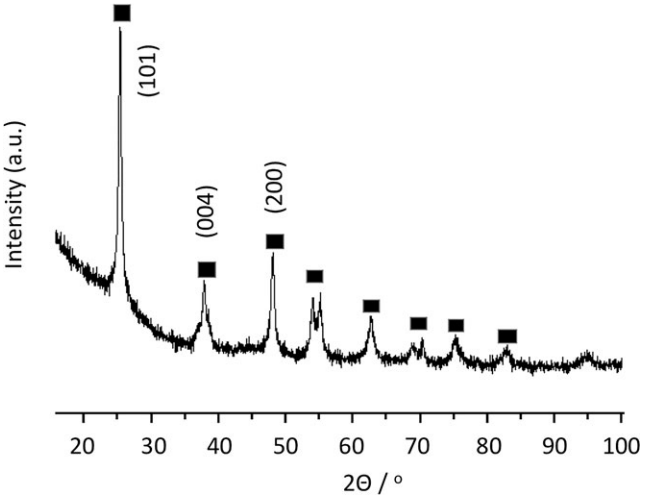

Fig. 1. XRD pattern of TiO_2–SiO_2/chitosan powder.

SEM

SEM analysis was carried out to observe the surface morphology and particle size of the TiO_2–SiO_2/chitosan powder. Figure 2(a) shows the surface morphology of the TiO_2–SiO_2/chitosan powder. The SEM pattern of the powder confirmed that the particle shapes were generally spherical. It is known that a particle is an agglomeration of several crystals. SEM analysis showed that the particle size of TiO_2–SiO_2/chitosan was in the range 125–375 μm. When compared to the size of the crystals obtained from the Scherrer's equation in XRD analysis, the particle size of TiO_2–SiO_2/chitosan is more than 10 times the size of the crystals.

SEM characterization was also performed to show the difference in surface morphology of cotton textile fibers coated with TiO_2–SiO_2/chitosan and those without coating. In addition, this characterization was carried out to observe the distribution of the TiO_2–SiO_2/chitosan powder on the surface of cotton fiber textiles and effect of the silane compound that acts as a hydrophobization agent on the surface of the textiles.

Figure 2(b) shows the surface morphology of the cotton fibers coated with TiO_2–SiO_2/chitosan. It is clear from the figure that there are several clusters of particles that attach to the surface of the cotton fibers. It could be confirmed that the clusters are particles of TiO_2–SiO_2/chitosan. For comparison, Figure 2(c) shows the morphology of cotton fibers coated with TiO_2–SiO_2/chitosan and made hydrophobic using HDTMS. It is seen that the powder is almost invisible on the textiles. This is because the textile is covered by HDTMS. However, the silane network formed by HDTMS did not completely cover the pores of the textiles. A network of silane compounds can be formed when HDTMS is heated up to 120 °C for 3 h. In this condition, HDTMS is assumed to be degraded because of the heating process.

UV-DRS

UV-DRS analysis was conducted to determine the optical properties of the TiO_2–SiO_2/chitosan powder. Figure 3 shows the UV-DRS pattern of TiO_2–SiO_2/chitosan. From the figure, it is seen that TiO_2–SiO_2/chitosan has an energy gap of ~3.03 eV. Because this compound has an energy gap ranging from 3.0 to 3.4 eV, this material tends to absorb UV light for

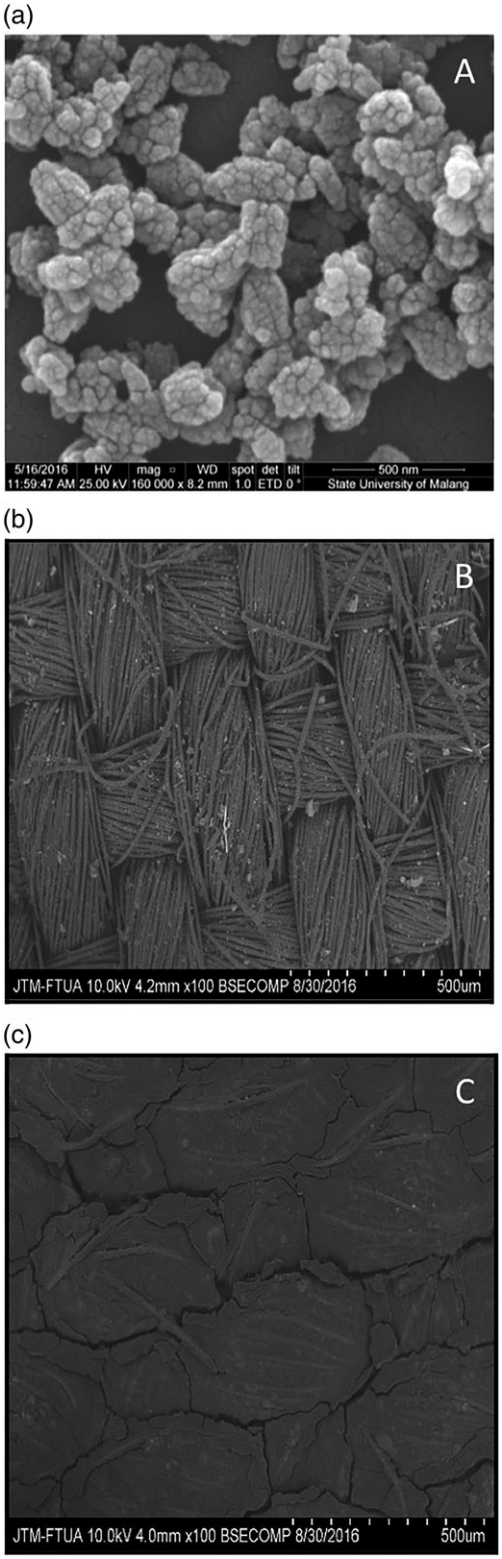

Fig. 2. SEM images of (a) TiO_2–SiO_2/chitosan, (b) textiles coated with TiO_2–SiO_2/chitosan, and (c) textiles coated with TiO_2–SiO_2/chitosan and HDTMS.

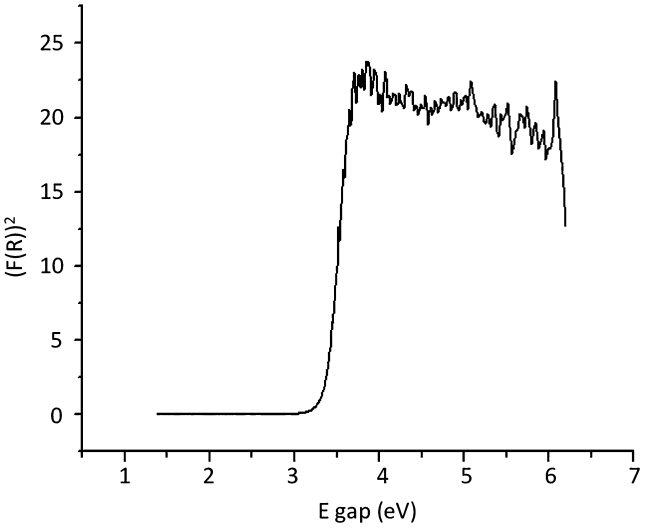

Fig. 3. UV-DRS spectrum of TiO_2–SiO_2/chitosan.

photocatalysis. Conversion from the energy gap to wavelength was then carried out using Planck's equation:

$$E = \frac{hc}{\lambda} \tag{1}$$

with h the Planck constant, λ the wavelength, and c the speed of light. This study confirmed that TiO_2–SiO_2/chitosan has a maximum absorption at 409 nm.

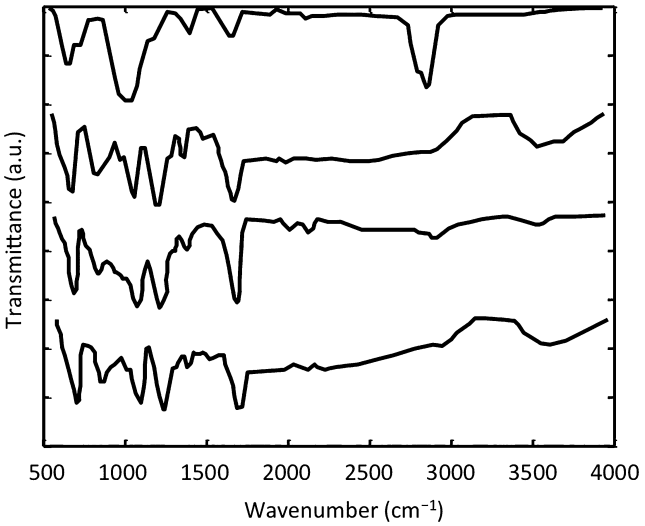

Fig. 4. FT-IR spectra of cotton textiles (a) without coating, (b) coated with BTCA, (c) coated with BTCA and TiO_2–SiO_2/chitosan, and (d) coated with BTCA, TiO_2–SiO_2/chitosan powder, and HDTMS.

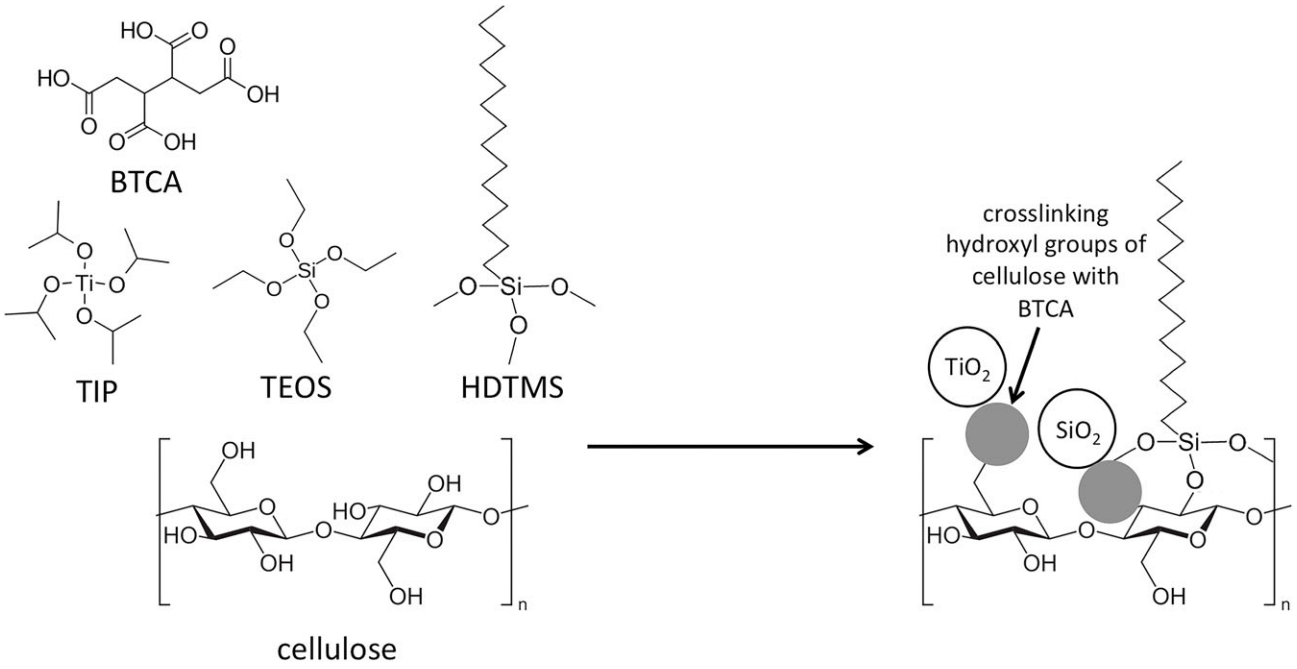

Fig. 5. Mechanism of action of HDTMS coated on the modified textiles.

FTIR pattern

FTIR patterns of all modified textiles are shown in Figure 4. There are six peaks in the figure. They are at wave numbers around 700–1050 cm^{-1}, which can be assigned to the Si–O group. The S–CH_3 group can be identified by the peak at 1250 cm^{-1}. Also, obvious peaks corresponding to C⊠O stretching are seen at ~1700 cm^{-1}. Moreover, the FTIR peak at 2900 cm^{-1} is associated with the functional groups C─H stretching of the long hydrocarbon chains in HDTMS. The general HDTMS coating mechanism is shown in Figure 5.

Hydrophobic properties

Another property of textiles was examined by measuring the hydrophobic surface WCA. It is well established that a material can be defined as hydrophobic if its WCA ≥ 90° while it is superhydrophobic if WCA ≥ 150°. Hydrophobization using HDTMS, which is a kind of silane compound with a long carbon chain, can make the surface of the material nonpolar.

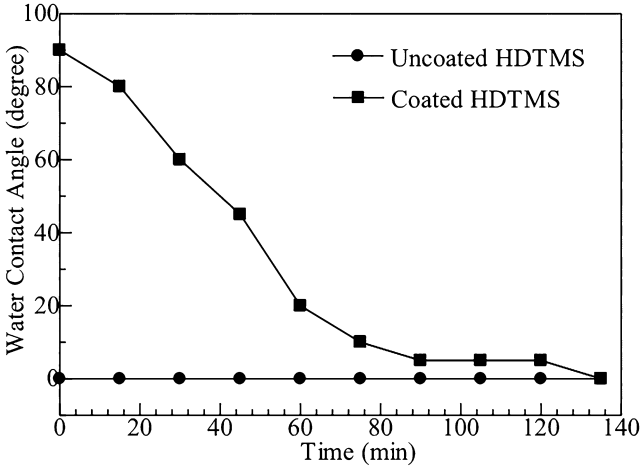

Fig. 6. Water contact angle stability on the modified textile.

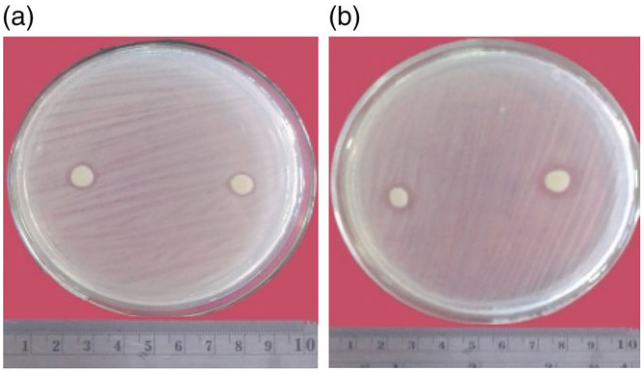

Fig. 7. Zone of inhibition of (a) textiles coated with TiO_2–SiO_2/chitosan and (b) textiles coated with TiO_2–SiO_2/chitosan and HDTMS against *E. coli*.

When cotton textiles are coated with both TiO_2–SiO_2/chitosan and HDTMS, they have the potential to acquire hydrophobic properties. The patterns of water droplets on the surface of cotton fibers coated with TiO_2–SiO_2/chitosan without HDTMS and with HDTMS are shown in Figure 6. It can be seen that the cotton fibers coated with TiO_2–SiO_2/chitosan but without HDTMS are hydrophilic with the WCA = 0°. In comparison, the fibers coated with TiO_2–SiO_2/chitosan and HDTMS are hydrophobic with WCA = 90°. This confirms that the hydrophobicity of the cotton fiber was increased by hydrophobization using HDTMS.

The stability of water droplets on the hydrophobic textile surface was observed by investigating how long the WCA can be maintained. The WCA on the surface of textiles coated with TiO_2–SiO_2/chitosan without hydrophobization was stable during the observation. Conversely, an obvious pattern could be observed for the textiles with hydrophobization using HDTMS. We found that water droplets can survive on the surface of cotton fibers coated with TiO_2–SiO_2/chitosan with hydrophobization using HDTMS for 105 min (WCA > 0°), and afterward the WCA reached WCA = 0°.

Antibacterial properties

The antibacterial capability of all modified textiles was investigated against two types of bacteria, namely the Gram-positive *S. epidermis* and the Gram-negative *E. coli*. *S. epidermis* is the bacteria that is found on the human skin, especially on the feet, and can cause shoe odor. In contrast, *E. coli* is found in the human gut. These bacteria are pathogens that can cause various diseases such as diarrhea, vomiting, and nausea.

The antibacterial capability of the modified textiles against *E. coli* and *S. epidermis* is shown in Figure 7. Figure 7(a) shows that the textile coated with TiO_2–SiO_2/chitosan has an inhibition zone of 9.60 mm when tested against *E. coli*. As a comparison, the textile cotton fiber coated with TiO_2–SiO_2/chitosan and HDTMS shows an inhibition zone of 10.41 mm (see Figure 7(b)). In addition, textiles coated with TiO_2–SiO_2/chitosan and HDTMS have the largest zone of inhibition when tested against *S. Epidermis*. This is evidence that the hydrophobization proposed in this work enhances the antibacterial capability of the textiles. We have thus proved that hydrophobization can improve the antibacterial capability. This can be attributed to the fact that hydrophilization repels water, thus reducing the amount of water on the textile surface.

For a complete overview, Table 1 lists the zone of inhibition of all modified textiles. In addition, the inhibition zone of textiles coated with TiO_2–SiO_2/chitosan powder is larger than that of textiles coated with SiO_2/chitosan and TiO_2/chitosan. Moreover, we have also proved that textiles without TiO_2–SiO_2/chitosan modification have the smallest zone of inhibition compared to others.

Table 1. Zone of inhibition of the modified textile against *S. epidermis* and *E. coli*

Textile	Zone of inhibition (mm)	
	S. epidermis	*E. coli*
TiO_2–SiO_2/chitosan	19.81	9.60
TiO_2–SiO_2/chitosan + HDTMS	22.87	10.41
TiO_2/chitosan	7.90	7.75
SiO_2/chitosan	7.00	6.90
HDTMS	2.20	1.42

CONCLUSIONS

The aim of this work was to evaluate the antibacterial capability of the cotton textiles coated with TiO_2–SiO_2/chitosan and HDTMS. The XRD pattern of TiO_2–SiO_2/chitosan confirmed the anatase phase structure with a tetragonal geometry having *hkl* (1,0,1), (0,0,4), and (2,0,0). Hydrophobization using HDTMS made TiO_2–SiO_2/chitosan invisible on the textiles. In addition, this study has confirmed that TiO_2–SiO_2/chitosan has maximum absorption at 409 nm. FTIR characteristics confirmed the molecular bonding on the textiles surface. We also found that the WCA of textiles coated with TiO_2–SiO_2/chitosan with and without HDTMS are 0° and 90°, respectively, identifying them as hydrophobic textiles. In general, this study has successfully proven that hydrophobization using HDTMS on the modified textiles can increase their antibacterial capability.

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