Antifungal property of cotton fabric textile: Modification of cotton fiber functions by coating compounds of TiO$_2$-SiO$_2$/Chitosan

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ABSTRACT

The antifungal activity from cotton fabric textile was studied by using TiO$_2$-SiO$_2$/Chitosan, with CTABr (Cetyl Trimethyl Ammonium Bromide) template as nanoparticle suspension disperser in the surface of cotton fabric textile. The difference of dip-spin coating time was correlated by the perfection of TiO$_2$-SiO$_2$/Chitosan coating and indicated by the gain of textile mass, stable to the washing and the ability of textile to inhibit the Aspergillus niger growth. Result showed that in the 24 h and 90 min of dip-spin coating, there was 14 mm of A. niger inhibition zone, compared with cotton fabric textile without treatment and was larger inhibition zone than cotton fabric textile treated by ketokonazol as a positive control. The chemical change occurred in the textile fiber after TiO$_2$-SiO$_2$/Chitosan coating was analyzed by FT-IR and SEM-EDX.

Keywords: antifungal, cotton, textile, TiO$_2$, SiO$_2$, Chitosan

INTRODUCTION

Textile is primary need and must be provided in daily activity. The need of high quality textile is needed by consumer. In order to choose the quality of textile for its use, consumers have to know the basic knowledge about textile fiber to make it easier to identify the high quality textile for daily need [1]. Based on the type of fiber, textile can be classified as cotton, wool and silk [2]. Cotton is a popular textile product, made from cotton fiber with cellulose as primer component. Cotton has unique properties such as soft and light fiber, numb and easy in maintenance. Cotton fiber has porous so it absorbs sweat easily. This property gives the opportunity for microbe to grow in textile fiber [3].

The microbial growth is stimulated by the structure of fiber and environment [4,5]. The presence of microbes in the fiber can cause cross infection, color degradation and bad odor to textile [4]. The need of clean a hygiene textile is urgent due to the raise of infection caused by pathogenic microbe. Several techniques have been applied to push the growth of microorganism by using chemical compounds or physical interaction such as the polymerization of N-halamin monomer to textile fiber, the addition of N-halamin to electro spinning, enzyme immobilization (eter crosslinked), the placement of ammonium salt to fiber textile covalently [6].

The application of nanotechnology to small industries by the coating of nanomaterial compounds (metal oxide) is to modify the function of textile fiber. Nanotechnology can increase the quality of textile to be the multifunction textile product with complex properties (anti microbial, UV protection, and anti odor). The success of nanotechnology application in textile industry has several advantages such as durability, multifunction without degrade the basic properties such as process ability, flexibility and economic.
TiO$_2$-SiO$_2$/Chitosan nanoparticle is a semiconductor, inert, non-toxic and photo catalytic material [7]. It also has anti fungal property because in UV radiation, there is redox reaction in band gap (valence a conduction band) which causes the release of radical hydroxyl and reactive oxygen species (ROS) [8,9]. The radical of hydroxyl can activate microbe by oxidizing phospholipid in membrane cell, where OH radical has ability to oxidize 1.000 – 10.000 times more effective than the inhibition ability of disinfectant in market such as chlorine, ozone and chlorine dioxide [10]. The application of TiO$_2$-SiO$_2$/Chitosan as anti fungal are safe for consumer, easy to apply in textile industry, economical value, compatible with other finishing agents and environmentally friendly. Rilda et al. 2015 [11] has synthesized TiO$_2$-SiO$_2$/Chitosan nanoparticle by modification with chitosan which can increase the photocatalytic activity and has good anti microbial property if doped with CTABr surfactant. Chitosan has non toxic, biocompatibility, biodegradability, anti fungal activity and chemical reactivity properties [12,13].

Fungi is a microbial species which can survive in high moisture textile. The growth of fungi can occur in both new and stored textile. The growth of textile is difficult to handle. Some chemical compounds which have been used to inhibit fungal growth can’t work effectively because the difficulty to degrade fungal cell. The use of TiO$_2$-SiO$_2$/Chitosan is an alternative solution to overcome the problem in textile because its effectiveness to any kinds of bacteria (positive and negative gram) [11,14,15]. The aimed of this research is to modify the function of textile fiber by TiO$_2$-SiO$_2$/Chitosan coating in preparation of anti fungal textile.

**MATERIALS AND METHODS**

**Materials**

Materials used were cotton textile (64 g/cm$^2$), chloride acid (HCl), Acetic acid (CH$_3$COOH), diethanol amine (C$_2$H$_5$N(OH)$_2$), isopropanol (C$_3$H$_6$O), tetraoxythorxy silicate (C$_5$H$_8$O$_2$Si), Salycilic acid (C$_7$H$_4$O$_2$COOH), Cationic surfactant (C$_{12}$H$_{25}$N(CH$_3$)$_3$Br) Merck, aquadest, titanium isopropoxide (C$_2$H$_5$O$_2$Ti) (Aldrich 97%), commercial chitosan (C$_6$H$_11$NO$_2$)$_n$ (85% de-acetylated).

**Synthesis and Preparation of Cotton Textile Coating by TiO$_2$-SiO$_2$/Chitosan**

TiO$_2$ sol suspension consists of the mixture of TIP, isopropanol and DEA as additive substance from TIP hydrolysis. SiO$_2$ as dispersion agent consists of the mixture of TEOS, isopropanol and HCl. The addition of chitosan/acetic acid at 5:1. Sol mixture was made by varying TiO$_2$ : SiO$_2$ molar composition (1:1 and 2:1) with the addition of CTAB surfactant as a template of particle distributor. The gel incubation was done at 110°C for 15 h. Gel was calcinated at 500°C for 3 h to get TiO$_2$-SiO$_2$/chitosan powder. TiO$_2$-SiO$_2$/Chitosan powder suspension was coated at 8x8 size of cotton textile which has been dipped in to acrylic acid solution. The dipping time variation were 6, 12 and 24 h. TiO$_2$-SiO$_2$/Chitosan coating (1:1 and 2:1) was done by dip-spin coating method with 60, 90, 120 and 150 min of time setting with CTABr as dispersion agent. The process was continued by the drying of cotton textile at 80°C for 10 min. The characterization of cotton textile was done by FT-IR, SEM and EDX analysis and non-coated cotton textile was used as a control.

**Anti Fungal Textile Measurement**

The suspension of *A. niger* which has been grown for 48 h in PDA medium was made by 10$^{-7}$ of dilution method. The suspension then inoculated into Petri dish with PDA medium and a piece of cotton textile (d= 10 mm) coated by TiO$_2$-SiO$_2$. Incubation was done for 48-72 h at 37°C in laminar flow with UV radiation.

**RESULTS AND DISCUSSION**

**The Gain of Textile’s Mass Analysis**

The analysis of the gain of textile mass is identical as a description that the coating of 8 x 8 cm textile with TiO$_2$-SiO$_2$/chitosan reached the perfection. Based on the duration of dipping time in acrylic acid binder for 6, 12 and 24 h, it was correlated to synergize the function of acrylic acid binder in TiO$_2$-SiO$_2$/chitosan coating to the textile fiber. Figure 1 describes the perfection of coating is related with the duration of dipping time in acrylic acid. The result showed that the dipping for 24 h has the highest gain of textile’s mass, which is indicated by the more of TiO$_2$-SiO$_2$/chitosan powder coating. The covalent bond of cross-linkester with hydroxyl group of cellulose formed in cotton fiber is relevant with the length of dipping process in acrylic acid and TiO$_2$-SiO$_2$/chitosan nanoparticle [16].
Figure 2 shows that there was a gain in textile’s mass after being coated by TiO$_2$SiO$_2$/chitosan with 60 to 90 min dipped with acrylic acid. Meanwhile, after dipped by acrylic acid for 24 h, there was a higher gain in textile’s mass. There was no significant gain in textile’s mass after dipped by acrylic aid for 120 – 150 min. It is predicted that there was a spreading of TiO$_2$SiO$_2$/chitosan suspension to the wall inside spin-coating instrument. The optimum time of TiO$_2$SiO$_2$/chitosan coating to the surface of cotton textile fiber is 90 min.

**Fig 2. The amount of textile cotton’s mass after being coated by TiO$_2$SiO$_2$/chitosan 1 % with Ti:Si molar composition 1:1 and 2:1 with 24 h dipped in acrylic acid**

**FT-IR Analysis**

FT-IR analysis can provide information that the perfection of textile fiber coating process with TiO$_2$SiO$_2$/chitosan is indicated by the formation of chemical interaction between hydroxyl group from cellulose with carboxylic group from acrylic acid as cross ink agent. This interaction happened was indicated by the change of the intensity of C=O stretching functional group at 1700 cm$^{-1}$ wave number [17].
Figure 3 shows that the intensity of ester covalent interaction which happened at 6 - 24 h of dipping process in acrylic acid was at 1427, 1160, 1109, 1054 and 1031 cm\(^{-1}\) of wave number are the indication of cellulose group comes from the fiber (Nasr, H.E, et al., 2009). Meanwhile, at 3 (c) spectrum, there is absorbance at 3000 and 1000 cm\(^{-1}\) which show C=O reside comes from CO\(_2\) at measurement time [18]. The intensity of C=O stretching group at 1700 cm\(^{-1}\) will be higher depends on the length of dipping time in acrylic acid binder which show the perfection of covalent interaction of ester. This also indicates the perfection of TiO\(_2\)-SiO\(_2\)/chitosan coating in the textile fiber.

If the coating time of TiO\(_2\)-SiO\(_2\)/chitosan was varied at 90 – 150 min, there was no significant changes in the intensity of C=O group. There was only minor shift of Ti-O-C interaction at 1260 cm\(^{-1}\) [17]. Meanwhile, the absorbance band at 1105 - 950 cm\(^{-1}\) was identical with the formation of Ti-O-Si interaction (Rilda, et al., 2014). It was also confirmed that there was O-Ti-O interaction at 650 cm\(^{-1}\) and vibration of Si-O-Si at 1080 cm\(^{-1}\) [19].

**Morphology and EDX Analysis**

SEM analysis can provide the surface morphology of cotton fiber which have been coated by TiO\(_2\)-SiO\(_2\)/chitosan. Figure 5 (a) shows the surface morphology of cotton textile after dipped in acrylic acid for 24 h. It can be seen that
the cotton fiber was soft and clean. The surface morphology of textile cotton which has been coated by TiO$_2$-SiO$_2$/chitosan (2:1) is shown at figure 5 (c), (d) and (e) with 6, 12 and 24 h of time variation of dipping in acrylic acid. It can be seen that textile cotton coated by TiO$_2$-SiO$_2$/chitosan with 24 h of dipping time in acrylic acid was coated by TiO$_2$-SiO$_2$/chitosan particle perfectly with well distribution particle by CTABr as dispersion agent.

The molar composition of Ti and Si influence the TiO$_2$-SiO$_2$/chitosan coating process in textile. SEM analysis shows that in Ti:Si (1:1) molar composition, the coating particle was distributed well compared with Ti:Si (2:1). TiO$_2$ is an electropositive compound and if the Ti composition is higher than Si, it will produce more positive charge particles and increase the interaction between textile cotton fiber with TiO$_2$-SiO$_2$/chitosan nanoparticle [20]. Meanwhile, SiO$_2$ is a particle which will form core shell with TiO$_2$ to enlarge the surface area and porosity of TiO$_2$ to the fungal cell [21]. Therefore, the Ti composition in TiO$_2$-SiO$_2$/chitosan gave the influence in the inhibition ability of fungi. The surface morphology of textile cotton coated by TiO$_2$-SiO$_2$/chitosan with concentration variation (Figure 5 f –h) showed that the significant difference of the amount of TiO$_2$-SiO$_2$/chitosan coated in the textile cotton which is correlated with EDX data.

The stability of TiO$_2$-SiO$_2$/chitosan coating on the surface of textile fiber can be measured by repetition rinse. Table 2 shows that there was the decrease of textile’s mass after repetition rinse.

<table>
<thead>
<tr>
<th>Repetition of Rinsing</th>
<th>Textile Cotton’s Mass Before Rinsing (g)</th>
<th>Mass Decreasing (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1767</td>
<td>1.75</td>
</tr>
<tr>
<td>3</td>
<td>0.1767</td>
<td>2.72</td>
</tr>
<tr>
<td>5</td>
<td>0.1767</td>
<td>2.99</td>
</tr>
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Figure 6 shows the effect of rinsing to the stability of coating on the textile fiber. Karimi et al. reported that the rinsing of textile cotton can decrease the mass of TiO$_2$ coated on the cotton fiber [16]. Meanwhile, Yu Ming et al. reported that TiO$_2$ nanoparticle is stable on the surface of textile cotton with 30 x rinsing by using cross-link poly(2-hydroxyethyl acrylate) (PHEA) [21].
EDX analysis can be correlated with the substance composition as an indication of the TiO$_2$-SiO$_2$/chitosan coating on the surface of textile cotton. Diffractogram pattern from Figure 7 (a) shows the composition of textile cotton without treatment. There was only substances from cellulose identified such as C and O. Figure 7 (b) shows the pattern of composition of textile cotton after dipped in acrylic acid. Acrylic acid is one of carboxylic acid with C$_3$H$_4$O$_2$ of molecular formula. There was increasing of C and O percentage of textile fiber after treated with acrylic acid to the non treated cotton. Figure 7 (c) shows the cotton textile coated by TiO$_2$-SiO$_2$/chitosan (1:1) consists of Ti and Si and is confirmed that it has been coated by TiO$_2$-SiO$_2$/chitosan. The capacity of TiO$_2$-SiO$_2$/chitosan on the surface of 8x8 cm textile fiber, by comparing the ability of powder suspension at 1 % concentration, was distributed well on the fiber surface. The loading capacity of the textile cotton to the TiO$_2$-SiO$_2$/chitosan at 1:1 was higher than 2:1.

**Antifungal Activity**

The antifungal activity of textile was measured by measuring the growth inhibition of *Aspergillus niger*. Figure 8 shows that the textile activity was influenced by the duration of textile dipped into acrylic acid binder and coating of textile cotton by TiO$_2$-SiO$_2$/chitosan with different of Ti and Si composition. The result shows that the inhibition...
ability of textile to *Aspergillus niger*’s growth was correlated to the amount of TiO$_2$-SiO$_2$/chitosan coated on the textile fiber and the gain of textile’s mass.

Figure 8. The inhibition zone of antifungal activity of textile to *A. Niger*: (a) non treated textile (control -); (b) textile treated by ketokonazol (control +); (c) textile coated by TiO$_2$-SiO$_2$/chitosan (1:1) and (d) textile coated by TiO$_2$-SiO$_2$/chitosan (2:1)

Figure 9 shows the antifungal activity of TiO$_2$-SiO$_2$/chitosan to *A. niger* with different composition variation of TiO$_2$-SiO$_2$/chitosan. Figure 9 (a) is a negative control which was non coated textile and it can be seen that there was no inhibition zone formed. Figure 9 (b) is a positive control which was textile coated by ketokonazol antibiotic and there was inhibition zone formed. Figure 9 (c) and (d) is textile coated by TiO$_2$-SiO$_2$/chitosan with each composition (1:1) and (2:1). It can be seen that the antifungal activity of TiO$_2$-SiO$_2$/chitosan with UV irradiation was higher than ketokonazol. The formed inhibition zones in textile coated by TiO2-SiO2/chitosan were 14 mm and 12 mm. In the composition Ti and Si (2:1), where the amount of TiO$_2$ is higher than SiO$_2$, the ability of TiO$_2$-SiO$_2$/chitosan to form free radical hydroxyl (•OH) and superoxide anion (•O$_2^-_{}$) is higher than TiO$_2$-SiO$_2$/chitosan compound with Ti:Si (1:1) composition. Free radical hydroxyl (•OH) and superoxide anion (•O$_2^-_{}$) are strong oxidator which are able to destroy the membrane cell of fungi which caused the lysis that inhibit the fungal growth.

Figure 9. The morphology of *Aspergillus niger*: (a) before coated by TiO$_2$-SiO$_2$/chitosan (1:1) and (b) after coated by TiO$_2$-SiO$_2$/chitosan (2:1)

*A niger* has the membrane cell which consists of chitin which is a complex compound and protective spore to the contamination. This causes *A. niger* is more difficult for cell lysis by the interaction with TiO$_2$-SiO$_2$/chitosan. The morphological structure of *A. niger* after inhibited by TiO$_2$-SiO$_2$/chitosan is shown at figure 9.
CONCLUSION

The effect of the time setting of dipping in acrylic acid was to allow the synergy among functional groups in the formation of cross-link. The optimum time resulted were 24 h and 90 min. FT-IR analysis showed that there was change in the C=O stretching intensity which is identical with chemical interaction of ester covalent bond. The surface morphology analysis by SEM-EDX showed that TiO$_2$-SiO$_2$/chitosan (1:1) nanoparticle was distributed well by CTABr role. Antifungal textile activity showed that the textile coated by TiO$_2$-SiO$_2$/chitosan (2:1) had higher inhibition ability which was 14 mm after irradiated with UV (536 lux) for 48 h. The stability of TiO$_2$-SiO$_2$/chitosan was done by the 5 times repetition of rinsing process. It can be concluded that this study can be applied to small industries due to the simple treatment.

Acknowledgments
This research was supported by The Ministry of Research, Technology and University through Competitive Grant Research Fund, LPPM University of Andalas, Padang, contract number of 030/SP2H/PH/RIT. SMLITABMAS /11/2015.

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