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Preparation Hydrophobic Fabric Coated by TiO₂ and Hexadecyltrimethoxysilane

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Abstract. In this research, hydrophobic fabric was prepared using TiO₂ and hexadecyl trimethoxysilane (HDTMS). The method of coating was layer by layer. First layer was coated with TiO₂ to increase the roughness and the second layer was coated with HDTMS to increase the hydrophobicity. The fabrics that has been coated TiO₂ has a water contact angle about 54.55°, while the fabric that has been coated HDTMS has a water contact angle about 109.79°. In this research, we studied the influence of deposition time and composition of TiO₂ and HDTMS. The result showed the optimum deposition time of TiO₂ about 60 and 30 min, the optimum concentration of TiO₂ and HDTMS about 0.4 and 0.1 M. This optimum condition exposed the water contact angle 135.93°. Characterization of the hydrophobic fabrics was done using IR-ATR showed the wave number of 667.2 cm⁻¹ and 893.1 cm⁻¹ were Ti-O-Ti and Ti-O-Si bond. The result of separation efficiency hydrophobic fabric of the mixture (cooking oil-water, toluene-water, chloroform-water, and hexane-water) were 93.30%, 84.61%, 61.54%, and 23.07%. The hydrophobic fabric was stable towards ambient temperature till 6 weeks, but unfortunately, it was not stable towards detergent.

Keyword : Hydrophobic Fabric, TiO₂, Hexadecyltrimethoxysilane

1. Introduction

Fabric is a textile material that is widely used in life daily. Cotton is a type of fabric that is considered to have a lot of fiber. Cotton fabric fibers contain the most abundant polymers in nature, namely cellulose. Various advantages of cotton fabric are flexible, have softness natural, good ability to absorb water, and cheap production costs [14]. Therefore, cotton fabrics are most in demand in the industry textiles and others. At present, hydrophobic fabrics from coating materials have developed sol-gel. This innovation arises because of intensive demands for creating hydrophobic fabric coatings [8].

During this time, the hydrophobic surface has attracted much attention academy and industry because of its unique characteristics such as unsticking, uncontamination, and self-cleaning [16]. In research previously [4], wood substrates were coated with silica nanoparticle which is modified with vinyllethoxysilane is used to create hydrophobic surface with a contact angle of 154°. Besides research accordingly, [12] used a fabric coated with SiO₂ and TiO₂ modified with hexadecyltrimethoxysilane via sol-gel method for creating a hydrophobic surface with a contact angle of 152°.

Hydrophobic properties can be obtained with two conditions, namely the surface rough and low surface energy. One way to improve surface roughness is to do TiO₂ deposition. Surface rough can also be obtained from materials with low surface energy or modify it with compounds that have low surface energy. Several types of compounds with groups -CF₃, -CF₂, -CH₃, and -CH₂ can be proven lower surface energy. However, the use of group compounds fluorocarbon is a major concern for the environment due to several effects generated from these compounds such as environmental pollution and toxicity the height of the compound. One of the chemicals used for replacing fluorocarbon is alkylsilane such as methyltrimethoxysilane (MTMS), octyltrimethoxy silane (OTMS), hexadecyltrimethoxysilane (HDTMS), and octadecyltrimethoxysilane (ODTMS) [15]. Modification of compounds silica-based with silane compounds such as HDTMS as surface energy low will produce a surface with hydrophobic properties. [13] have done research by improving hydrophobicity of wood material modified with HDTMS-TiO₂. On the study used several variations of concentration from TiO₂ (0.2-5%) and HDTMS (0.2-3%). The contact angle resulting from TiO₂ coating is at 91° and



coating with HDTMS-TiO₂ produces contact angles amounting to 138°. The combination of TiO₂ and HDTMS in the study has a contact angle value is less than 150° which states that the addition HDTMS gives effect to the hydrophobic surface of wood.

In this study a hydrophobic fabric was used for separation of non polar compounds (cooking oil, toluene, chloroform, and hexane) with water. Hydrophobic fabric preparation is studied through variations in deposition time TiO₂, HDTMS, and variations in TiO₂ concentration, HDTMS by dip coating method by layer by layer. HDTMS compounds are used to replace fluorocarbon compounds which are toxic as hydrophobic agents. Carbon chain the length of HDTMS is expected to reduce the surface energy of the layer so that it can produce a hydrophobic fabric. Coating method chosen because it has a more even coating level. Selection of techniques layer by layer is a simple and easy technique to use to make thin layer films through layer deposition.

Non polar compounds used in this study are oil fried, toluene, chloroform, and hexane because all four have different hydrophobic characteristics. In this study, fabric hydrophobic test determined from the results of contact angle measurements. The sample is characterized using FTIR to determine the bond formed between Ti-O-Ti and Ti-O-Si and characterized using SEM to determine surface morphology before and after TiO₂-HDTMS coated.

2. Experimental Method

Fabric soaked in TiO₂ solution with a variation of deposition time 1, 5, 30, 60, 120, and 180 minutes. The cloth is dried at 70 °C for 30 minutes, after drying it is soaked in HDTMS solution for 5 minutes and dried at 70 °C for 30 minutes. The fabric is measured with the contact angle use the Image-J application.

Fabrics were soaked on TiO₂ soles during TiO₂ optimum deposition time, fabric then dried for 30 minutes at 70 °C. Fabric soaked in soles HDTMS with variations in deposition times 1, 5, 30, 60, and 90 minutes. Fabric dried at 70 °C for 30 minutes and measured contact angle by using the Image-J application.

This study uses five variations of TiO₂ concentration, namely 0.15, 0.3, 0.4, 0.8, and 1 M. This coating uses the layer by layer method with dip the cloth into the TiO₂ sol with a variation of concentration of 0.15, 0.3, 0.4, 0.8, and 1 M during the optimum deposition time obtained. The cloth is soaked into the HDTMS soles with optimum deposition time obtained. The cloth is dried at 70 °C for 30 minutes and the contact angle is measured using the Image-J application.

In this study there were three variations of HDTMS concentration, namely 0.05, 0.1, and 0.2 M. Fabric soaked in TiO₂ soles during the optimum TiO₂ deposition time, the fabric is then dried for 30 minutes at 70 °C. After that, cloth immersed in a variation of 0.05 HDTMS sol, 0.1 and 0.2 M during optimum time HDTMS and dried again for 30 minutes at 70 °C.

Hydrophobicity test in this study through the absorption process. Compound non polar used in his study is cooking oil, chloroform, toluene, and hexane with the same treatment. The piece of cloth that has been coated with TiO₂-HDTMS dipped in a mixture of aqueous solutions and compounds non polar. The solution mixture consists of 0.2 mL of non polar compounds and 0.6 mL water. Then calculate the efficiency of the separation of non-polar and water compounds of the three samples.

Determination of the stability of the fabric that has been coated with TiO₂-HDTMS detergent is done by soaking the cloth for 5, 10, and 15 minutes detergent. The cloth is dried for 30 minutes at 70 °C. Next, cloth the contact angle is measured using Image-J.

The determination of the stability of the fabric that has been coated with TiO₂-HDTMS is carried out by letting the cloth on the outside air for 6 weeks. Contact angle is measured within 1 week.

3. Results and Discussion

In this study TiO₂ sol preparation refers to the procedure conducted [10]. The material used consists of tetrabutyl orthotitanate (TBOT) as a source of titanium, ethanol and water as a solvent and hydrolysis of TBOT, and concentrated HCl as a catalyst. Acid catalysts are chosen because hydrolysis under acidic conditions can accelerate the occurrence of protonation, so silicon groups that have electrophilic properties are more susceptible to attack by clusters OH [7].

TiO₂ sol preparation is done by dissolving TBOT into a glass beaker containing ethanol, 1M HCl, and distilled water then heated at a temperature 60 °C and stirred for 1.5 hours to form a cloudy white solution. Then it is allowed to cool until the solution cools and the concentrated HCl drops are added

by drop until it forms transparent or non colored TiO_2 soles.





In this study HDTMS sol preparation refers to the procedure conducted [3]. HDTMS sol preparation is done with mixing ethanol, HDTMS, and acetic acid. The mixture is then stirred for 60 minutes and form a colorless sol.

The source of silica in the manufacture of soles is produced by HDTMS, ethanol serves to hydrolyze HDTMS to form alkylsilanols and acids acetate is used as a catalyst. HDTMS is used to increase angles contact with coating the fabric substrate, because HDTMS compounds have chains length that can bind to silica particles causing energy the surface is lower and causes the contact angle to increase [11].

Fabric preparation is carried out by sonication of the fabric in ethanol for 30 minutes. The purpose of sonication in ethanol is to clean the fabric from dirt. Coating of the fabric substrate is done with a layer by layer (LBL) model.

This study uses a cloth substrate, because the fabric is a substrate porous so it has certain adsorption abilities. Adsorption ability this is studied by varying deposition time. Effect of deposition variations TiO_2 deposition time was studied with a time of 1, 5, 30, 60, 90, 120, and 180 minutes. Variation in deposition time is done to determine the optimum time of TiO_2 coating on fabric. Fabric contact angle before and after TiO_2 coating and HDTMS are shown in Table 1.

Table 1. Fabric contact angle before and after coated TiO_2 and HDTMS

Fabric	Contact angle ($^\circ$)	Figure
Before coated	0	
Fabric + TiO_2	54.55	
Fabric + HDTMS	109.79	
Fabric + TiO_2 + HDTMS	135.93	

In Table 1 it is known the difference in contact angle that occurs in the fabric before and after TiO_2 and HDTMS coating. Fabric used in this study is a super hydrophilic fabric that requires modification to create a fabric to be hydrophobic. In this research modification of fabric using TiO_2 to create surface forces and HDTMS to reduce surface energy. Table 1 shows that the cloth that originally had a contact angle of 0° changed drastically 109.79° after the addition of silane namely HDTMS.

Variation of TiO_2 deposition time is done by immersing the cloth in sol TiO_2 with a time variation of 1, 5, 30, 60, 90, 120, and 180 minutes. Fabric then dried for 30 minutes. Next, the cloth is soaked in the sol HDTMS for 5 minutes and dried again. Fabric that has been coated TiO_2 and HDTMS are then measured contact angles using the application Image-J. Effect of TiO_2 deposition time on the contact angle of the coated fabric TiO_2 -HDTMS can be shown in Figure 1.

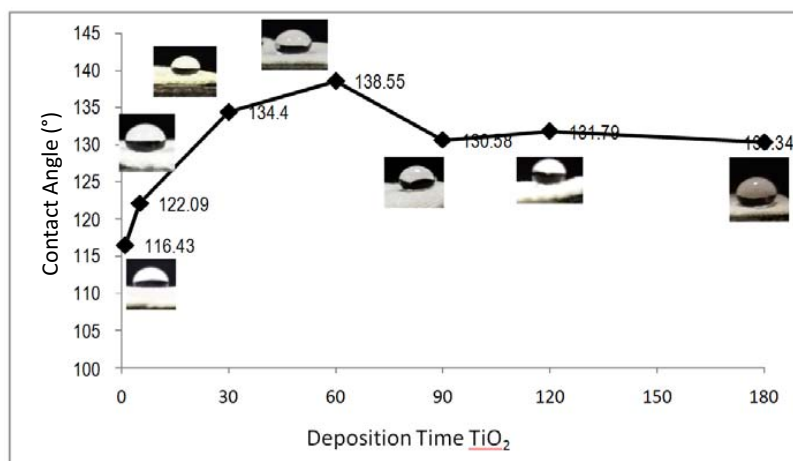


Figure 1. Effect of TiO_2 deposition time on the contact angle of the coated fabric TiO_2 HDTMS

From Figure 1 it is known that the longer the TiO_2 soaking time causing contact angles to increase. At 5-60 minutes it occurs the increase in contact angle is suspected due to increasing roughness thus causing the contact angle to increase, while in the 90-180 minutes there is a decrease in contact angle caused by the TiO_2 soles that have met all substrate surfaces so that the density of the hydroxyl group is increasing increases and causes the hydroxyl group to join the molecule water and form hydrogen bonds which can increase wet ability substrate so that the contact angle decreases [2]. With Thus, the optimum TiO_2 deposition time is 60 minutes. Optimum time TiO_2 deposition is then used to study the variation of deposition time HDTMS.

Variation in HDTMS deposition time is done by soaking the cloth in the TiO_2 sol during the optimum time obtained from the time variation TiO_2 deposition is 60 minutes. The cloth is dried for 30 minutes at 70°C , after that the cloth is soaked in HDTMS soles with a variation of time 1, 5, 30, 60, and 90 minutes. The cloth is then dried again for 30 minutes at a temperature 70°C . After finishing the coating on the fabric then the angle is measured contact using the Image-J application. Effect of time deposition variation HDTMS to fabric contact angles can be shown in Figure 2.

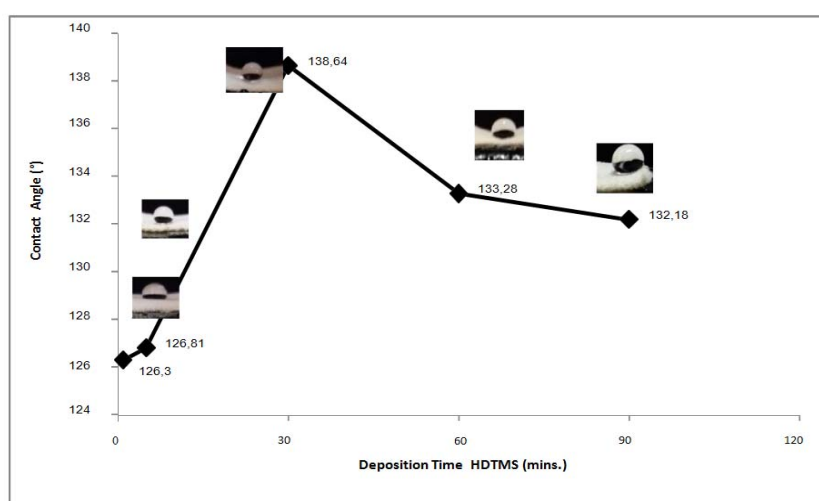


Figure 2. Effect of HDTMS deposition time variation on fabric contact angle TiO_2 -HDTMS

From Figure 2 it can be seen that the longer the immersion time HDTMS, the contact angle increases because cellulose is on the substrate the fabric is able to bind to the methyl group in silane

and will increase CH_3 groups that exchange with silanol groups. The length of the immersion process indicates the bond that occurs between the substrate and silane. In minutes 60-90 there is a decrease in contact angle that is suspected due to time ability absorption is no longer optimal which is indicated by the layer on the substrate is getting thicker so the layers are easily brittle and cause the substrate will be easily moistened so that it decreases the contact angle. With thus the optimum time for deposition time of HDTMS is 30 minutes. This optimum deposition time is used to study variations in TiO_2 concentrations.

Variations in TiO_2 concentration were carried out to determine the concentration optimum for hydrophobic fabric coating with TiO_2 -HDTMS. TiO_2 soles on hydrophobic fabric coating has a role to increase roughness surface, so that the optimum concentration in this study needs to be determined. The optimum concentration is determined from the concentration that produces angles highest contact.

In this study, variations in TiO_2 concentration were carried out in a way soaking cloth in TiO_2 with various concentrations of 0.15, 0.3, 0.4, 0.8, and 1 M during optimum deposition time obtained from TiO_2 and HDTMS that is 60 minutes and 30 minutes. The fabric measured the contact angle using Image-J. Effect of contact angle on variation of TiO_2 concentration on fabric coating The TiO_2 -HDTMS is shown in Figure 3.

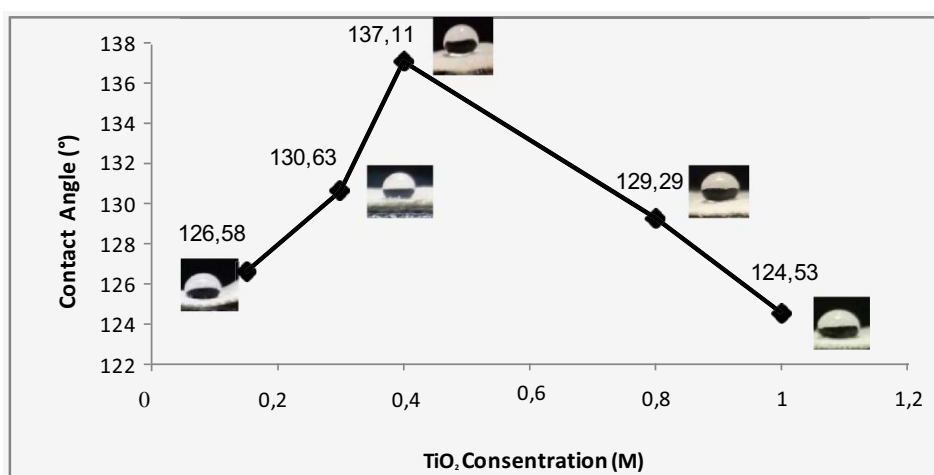


Figure 3. Effect of TiO_2 concentration variation on contact angle on TiO_2 -HDTMS fabric coating

Based on Figure 3, the fabric that has been coated with TiO_2 -HDTMS has hydrophobic properties. The higher the TiO_2 concentration causes the contact angle increased due to roughness on a high cloth substrate. At a concentration of 0.8-1 M there is a decrease in contact angle allegedly due to hydroxyl groups form a multi layer hydroxyl which results in an easier surface absorb water and decrease contact angle. Thus, concentration the optimum TiO_2 is 0.4 M which is indicated by the most contact angle high. The optimum concentration of TiO_2 is then used to study HDTMS concentration.

Variations in the concentration of HDTMS in this study to find out influence of HDTMS concentration on contact angle. That concentration used in this study is 0.05, 0.10, and 0.20 M. Selection of concentration 0.05, 0.10, and 0.20 M because if the concentration is greater than 0.20 M it will accelerate the sol process into a gel. Gelation time is an important factor because if the sol has become a gel, then the coating does not become homogeneous so that it can affect the contact angle. The contact angle values of variations in HDTMS concentration are shows that the effect of HDTMS concentration no significant effect on increasing possible contact angles caused by HDTMS forming a monolayer bond on silica particlesor on the surface of cotton fibers according to those reported [6].

FTIR characterization aims to find out the bonds that occur atfabric that has been coated with TiO_2 -HDTMS, especially the bond between Ti-O-Ti and bond Si-O-Ti. FTIR spectra without coating and TiO_2 -HDTMS fabrics are shown in Figure 4.

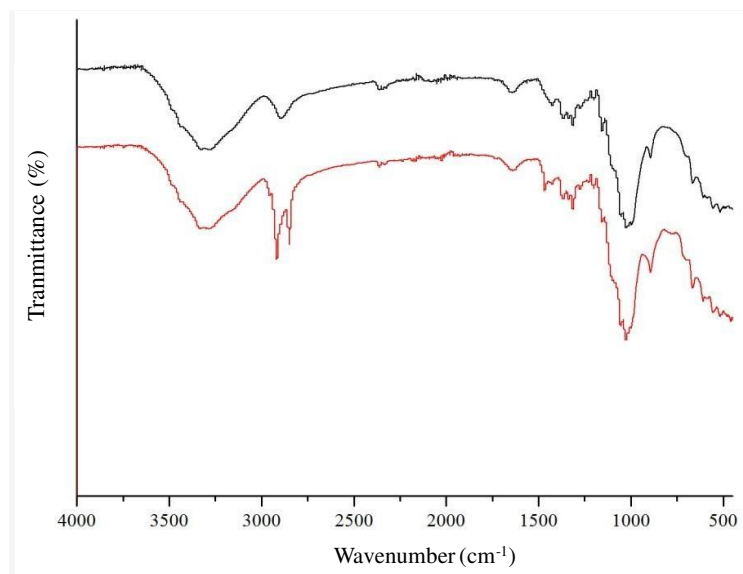


Figure 4. Spectra FTIR (a) non-coating fabric and (b) TiO_2 -HDTMS fabric

In Figure 4 there is a wide spectra at the wave number 3282.90cm^{-1} which indicates the presence of a $-\text{OH}$ group bond. The next spectrum is located at wave numbers $2849.44 - 2916.50\text{ cm}^{-1}$ which shows the existence CH_3 and CH_2 bonds which indicate the presence of long chain alkyl hydrophobic fabric surface caused by HDTMS soles. There is a Ti-bond O-Ti is shown in wave number 667.20 cm^{-1} which is vibration measure of Ti-O-Ti. This vibration appears at $800\text{--}400\text{ cm}^{-1}$ uptake [9]. The next wave number is at 893.09 cm^{-1} which indicates the presence of Ti-O-Si [1].

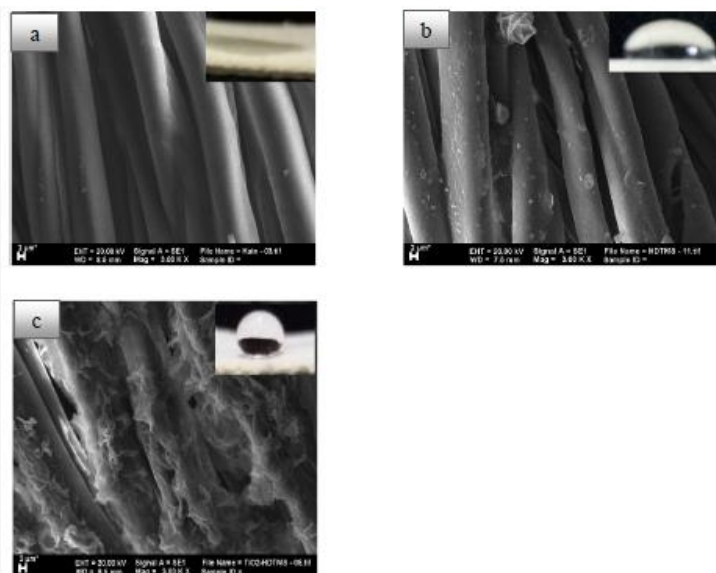


Figure 5. SEM fabric results (a) without coating, (b) HDTMS coated fabric, and (c) fabric coated with TiO_2 -HDTMS

SEM characterization was carried out to determine surface morphology on cotton cloth before and after coated with HDTMS and TiO_2 -HDTMS. Results morphological characterization of cotton fabric without coating is shown in Figure 5 (a), Figure 5 (b) morphology of HDTMS coated fabrics, and

Figure 5 (c) morphology images TiO_2 -HDTMS coated fabric. In Figure 5 (a) is a fabric morphology before it is done coating, in this picture clearly visible cellulose fibers from cotton cloth. In Figure 5 (b) is a morphology of cotton fabric coated with HDTMS, at the picture shows that there is a solid layer that has not been homogeneous in uniform cotton. Next in Figure 5 (c) is the cotton fabric morphology TiO_2 -HDTMS has been coated, in the picture cotton fibers are no longer clearly visible because the surface of the sample is covered by titania particles conditioned as a layer [5]. Modification of surface roughness fiber and low surface energy, causing the cloth to not be moistened by water droplets so that they have hydrophobic properties.

Value of the efficiency of the separation of non-polar and water compounds in this study shows that the value of efficiency the highest separation is a sample of cooking oil which has an efficiency value 93.30%, toluene 84.61%, chloroform 61.54% and hexane 23.07%.

Cooking oil has the highest separation efficiency value due cooking oil has a very small value of solubility to water caused the structure of cooking oil which is composed of unsaturated fatty acids so it is non polar and very easily separated from water. Difference in efficiency value separation of toluene, chloroform and hexane samples was also caused difference in water solubility. The higher the solubility value of a compound in water, it will be difficult to be separated, and vice versa the smaller the solubility value of the compound in water it is easier to separate. Hexane in terms of value solubility should be me the lowest efficiency value. This is because hexane is faster yawn.

In this study, absorption capacity shows that the fabric is TiO_2 -HDTMS has been shown to exhibit hydrophobic properties because it can resist water and only non-polar compounds. %Efficiency of separation cooking oil has high efficiency, but hexane has non polar and water compounds are shown in which can be absorbed. This hydrophobic fabrics can be used for absorbents that can absorb non-compounds polar.

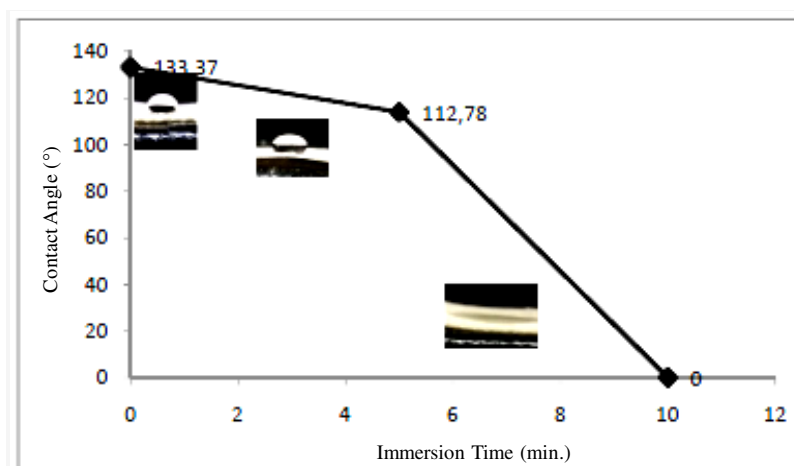


Figure 6. Effect of contact angle on detergent immersion that has been coated with TiO_2 -HDTMS

In this study, the stability of the hydrophobic fabric is carried out by soaking cloth using detergent. The cloth is dried in oven at a temperature of 70 °C fabric measured contact angle. The contact angle obtained is shown in Figure 6. In Figure 6. shows that the fabric substrate is modified with Silica soles and HDTMS are less stable, causing all the cloth to wet at 10 minutes soaking time.

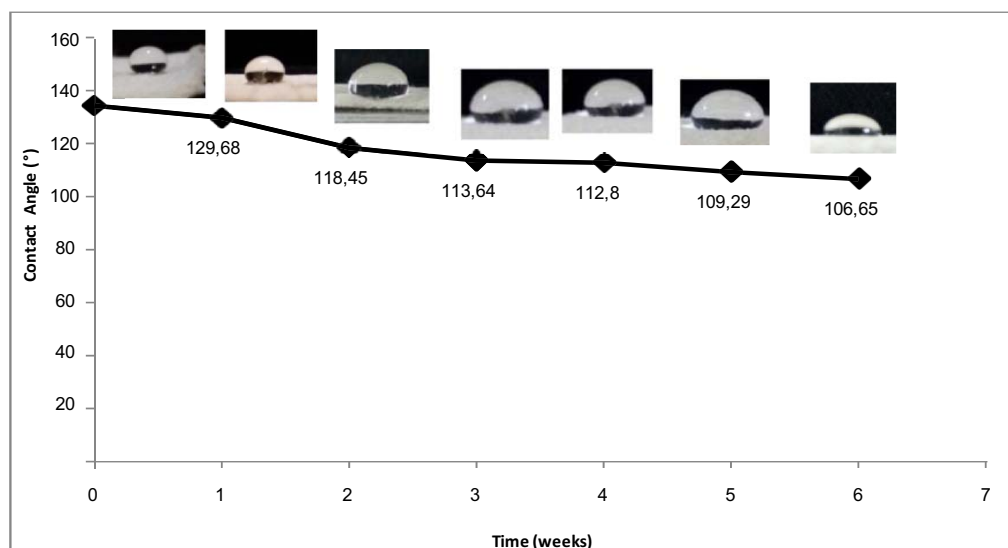


Figure 7. Effect of contact angle on fabric that has been coated with TiO₂-HDTMS in sunlight

The stability of the hydrophobic fabric when left under visible light shown in Figure 7. Testing hydrophobic fabric contact angle on stability under visible light is observed once a week for 6 weeks. In Figure 7 shows the longer the fabric is left in the sun causing the contact angle to decrease. Decrease contact angle allegedly caused because during exposure to sunlight the fabric accumulates contaminants. The fabric that has been coated with TiO₂-HDTMS in this study is still able to maintain its hydrophobic properties known from the point of contact ie > 90.

4. Conclusions

The longer of deposition time and the more high concentrations of TiO₂ and HDTMS cause contact angles on the fabric increases, but there is a decrease in contact angle on a certain time because the hydroxyl group tends to be dominant so that it can bind to water molecules and make surfaces absorb water. TiO₂-HDTMS coated fabric has the ability to separate non-polar compounds (cooking oil, toluene, chloroform, hexane) - water respectively 93.30%, 84.61%, 61.54%, and 23.07%. The stability of the fabric that has been coated with TiO₂-HDTMS is capable maintain its hydrophobic properties in the outside air for 6 weeks with water contact angle in the 6th week of 106.65°, whereas fabric that has TiO₂-HDTMS coated has low stability against detergents.

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