Synthesis and characterization of methyltriethoxysilane water repellent

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Abstract. Methyltriethoxysilane (CH₃Si(OH)₃) as a water repellent has been synthesized from trichloromethylsilane and ethanol by varying their composition, reaction condition, and the addition of nanosilica. The properties of the material have been characterized using FTIR for identification of raw materials and water repellent product, SEM for identification of water repellent coating surface, and tensiometer for measurement of water repellent contact angle. The FTIR spectra confirm the reaction of the water-repellent formation. The water repellent product was applied by spraying or dip coating on the automotive window surface. This study shows that the best ethanol composition is 91% and the best contact angle of synthesized water repellent material is 149.46°. This contact angle is higher than that of a commercial product, which shows it as a property of the superhydrophobic material. Water repellency properties increase as the composition of trichloromethylsilane increases. It shows that the increasing of trichloromethylsilane composition can also increase methyltriethoxysilane formation. However, glass surface becomes opaque as the composition of trichloromethylsilane increase because methyltriethoxysilane will create the Si-O-Si layer that has a white color. The addition of nanomaterial also increases the surface roughness, but a binder is required to bind nanomaterial to the water-repellent layer. For an application, dip coating has better water repellency than spraying. This is because dip coating method creates more homogenous nanomaterial precipitation on the surface. On the other hand, the level of transparency is worse. Therefore, the water repellent of trichloromethylsilane is recommended for applications that do not need clarity such as bathroom glass wall.

1. Introduction

Water repellent is a material having properties of rejecting water due to its high hydrophobicity. Hydrophobic material means that its surface tension less than 35 dyne/cm and its contact angle more than 90° (Arkles, 2006). Technically, water repellent can be made from both polymer and non-polymer to create low surface tension. In addition, it also uses nanotechnology to create large coating surface area. One of non-polymer material that can be made to be water repellent is silane, a chemical compound which has silicone as its structural center. Generally, the molecular structure of silane is YSiX₃ in which Y is organofunctional group and X is alkoxy or chloride group. Silane which consists of carbon-silicon bond (CH₂-Si) is well-known as organosilane (Mateer et al, 2012). The carbon-silicon bond is really stable, nonpolar, gives low surface tension and hydrophobic effect (Gao and McCarthy, 2006). In addition, silane is also the most frequently used commercial adhesion promoter.
(Harper and Petrie, 2003). Furthermore, silane will react easily with water and form silanol. Silanol can react with other silanol and form a very stable bond, siloxane (Si-O-Si). According to Gao and McCarthy (2006), trichloromethylsilane (TCMS) can be used to create a superhydrophobic surface.

Water repellent can also be made using lotus leaf effect that combines low surface tension and a large surface area in order to produce better hydrophobic properties, self-cleaning ability, and very rough surface. Hydrophobic properties can be generated by using a material, such as a polymer which creates low surface tension. Moreover, the rough surface can be generated by adding nanoparticle. Hydrophobicity can be determined by measuring contact angle between the water droplet and glass surface.

2. Experiment

2.1. Materials
Trichloromethylsilane (TCMS) was a commercial product from Alibaba (China), Nanosilica SiO$_2$ obtained from Center for Ceramics of Bandung (Indonesia), Sodium Silicate obtained from PT Ajidharma Mas Tritunggal Sakti (Indonesia), demineralized water, acetone, ethanol, and toluene were obtained from Department of Chemical Engineering, Institut Teknologi Bandung.

2.2. Functional Group Identification of Trichloromethylsilane
Trichloromethylsilane functional group was identified using Fourier Transform Infrared (FTIR) Spectrometer Prestige 21 Shimadzu. TCMS was dropped between two plates of Potassium Bromide (KBr) or Sodium Chloride (NaCl).

2.3. Synthesis of Methyltrihydroxysilane Water Repellent

2.3.1. Method I. Trichloromethylsilane mixed with ethanol under the acid condition in the fume hood to make 91 to 98% TCMS solution, with or without nanosilica. The concentration of the solution varied from 2 to 9%-mole TCMS with 1%-mass of nanosilica. Having stirred for 20 minutes at 30°C using magnetic stirrer, the solution was then sprayed twice into a glass which would be heated in the oven at 120°C within 10 minutes.

2.3.2. Method II. Trichloromethylsilane mixed with ethanol in order to make 1 M TCMS solution. Glass dipped and enclosed in the solution for one day. Following this, the glass was taken out and washed with toluene, ethanol and ethanol-water solution (1:1). Having washed, the glass was then heated in an oven at 120°C for 10 minutes.

2.4. Characterization of Methyltrihydroxysilane

2.4.1. Functional Group Identification. The functional group of trichloromethylsilane that has been reacted with ethanol identified using Fourier Transform Infrared (FTIR) Spectrometer Prestige 21 Shimadzu. The sample dropped between two plates of Potassium Bromide (KBr) or Sodium Chloride (NaCl).

2.4.2. Contact Angle Measurement. The contact angle of methyltrihydroxysilane water repellent measured with Attension Theta Lite pendant drop tensiometer. The water repellent was applied to a glass surface using a syringe. After that, the glass surface was installed to pendant drop tensiometer and the contact angle was determined using OneAttention software. The contact angle was determined using Young equation on the relation of surface tension between solid and liquid ($\sigma_{SL}$), solid and vapor ($\sigma_{SV}$), and liquid and vapor ($\sigma_{LV}$) which is shown at equation 1.

$$\sigma_{LV} \cos \theta = \sigma_{SV} - \sigma_{SL}$$  (1)
The Young model for water droplet on a solid surface is also shown in Figure 1.

2.4.3. Coating Surface Identification. Methyltrihydroxysilane water repellent coating surface was identified using Scanning Electron Microscope (SEM) JEOL-JSM-6510LV. The sample was put at specimen support and then was set in order to make the upper part of specimen same with holder top part. Following this, the specimen was observed using software integrated to the SEM.

3. Results and Discussion

3.1. Synthesis of Methyltrihydroxysilane Water Repellent

Methyltrihydroxysilane water repellent was synthesized from the following reactions between trichloromethylsilane and ethanol:

\[
\begin{align*}
\text{CH}_3\text{SiCl}_3 + 3 \text{C}_2\text{H}_5\text{OH} & \rightarrow \text{CH}_3\text{Si(OC}_2\text{H}_5)_3 + 3 \text{HCl} \\
\text{C}_2\text{H}_5\text{OH} + \text{HCl} & \rightarrow \text{C}_2\text{H}_5\text{Cl} + \text{H}_2\text{O} \\
\text{CH}_3\text{Si(OC}_2\text{H}_5)_3 + \text{H}_2\text{O} & \rightarrow \text{CH}_3\text{Si(OH)}_3 + 3 \text{C}_2\text{H}_5\text{OH}
\end{align*}
\]

In these reactions, ethanol acts as the reactant as well as TCMS solvent. Water repellent coating surface is very influenced by water presence. The more water composition, the more methyltrihydroxysilane \([\text{CH}_3\text{Si(OC}_2\text{H}_5)_3]\) was formed. As a result, the coating of the methyltrihydroxysilane water repellent gave white color surface.

3.1.1. Characterization of Water Repellent Synthesis Method I. The absorption band of Si-O group that binds glass surface and forms the Si-O-Si bond is around 800-900 cm\(^{-1}\). Based on Figure 2b, there is the Si-O group at trichloromethylsilane which is reacted with ethanol at 875 cm\(^{-1}\). It shows that methyltrihydroxysilane layer has been formed. Besides, Si-O group is also detected at trichloromethylsilane at peak 898 cm\(^{-1}\) (Figure 2a). This is caused by a spontaneous reaction between trichloromethylsilane and water in the air as follow:

\[
\text{CH}_3\text{SiCl}_3 + 3 \text{H}_2\text{O} \rightarrow \text{CH}_3\text{Si(OH)}_3 + 3 \text{HCl}
\]

In terms of composition variation, the bigger composition of trichloromethylsilane the more methyltrihydroxysilane generated. As a result, coating surface of the product will have more water repellent. However, the best contact angle of product generated based on the method I was still less than 90\(^\circ\). This means that the surface is not hydrophobic enough. Besides, increase of trichloromethylsilane concentration also increase the opacity of the glass. This is because methyltrihydroxysilane and glass generate Si-O-Si layer which has a white color. Figure 3 shows water droplet on the glass coated with the best product synthesized using the method I at 91% ethanol composition.
Figure 2. FTIR pattern of: (a) trichloromethylsilane; (b) trichloromethylsilane reacted with ethanol
There is also the addition of nanosilica at 1% of the total weight of ethanol and trichloromethylsilane. The generated surface color is also white. If it is wiped, the white color, as well as the water repellent, are disappeared. It shows that addition of nanosilica directly does not create a layer of a nanocomposite. Instead, nanosilica will settle on the glass surface, as well as inhibit the formation of the Si-O-Si bond. The best product of nanosilica addition is that with 91% ethanol compositions which can be seen in Figure 4.

In terms of sodium silicate addition, it seemed that methyltrihydroxysilane water repellent was not generated. Meanwhile, the reaction between trichloromethylsilane, ethanol, and sodium silica produced cross-linked silicate polymer and did not generate the Si-O-Si bond between glass and trichloromethylsilane.

3.1.2. Characterization of Water Repellent Synthesis Method II. Water repellent synthesized by method II generates homogenous solid white layer. Glass that has been coated by methyltrihydroxysilane water repellent has contact angle more than 90°, which is 149.46° (Figure 5). This contact angle shows that the glass surface is superhydrophobic. The water repellent is a result of closed reaction which makes the water content in the reaction small. The surface is also homogenous as result of the reaction process occurs in the glass dipped for one day.
Figure 5. The contact angle of water droplet on glass coated by methyltrihydroxysilane water repellent method II

The glass coated with methyltrihydroxysilane water repellent method II was identified by Scanning Electron Microscope (SEM) at the enlargement of 500 and 2000 times. It can be seen in Figure 6, methyltrihydroxysilane water repellent is layered and gives whiter color in the glass.

Figure 6. SEM surface morphology of glass coated by methyltrihydroxysilane water repellent method II: (a) enlarged 500 times; (b) enlarged 2000 times

3.2. Comparison of Synthetic and Commercial Product Performance

Figure 7. Water droplet on glass coated with: (a) commercial water repellent, RainZ Dura; (b) synthesis water repellent, methyltrihydroxysilane

Figure 7 shows that both commercial and synthetic product has hydrophobicity. Besides, the contact angle for the commercial product is less than 90°, while for the synthetic product is approximately 149.46°. Therefore, the performance of synthetic water repellent is better than commercial in terms of
contact angle and hydrophobicity. However, the transparency of the glass coated by both of them is different. The glass coated with commercial water repellent is transparent, while the glass coated with synthetic water repellent is opaque and white in color. By and large, synthesis water repellent is recommended for applications that do not need high clarity such glass wall of a bathroom.

4. Conclusion
Based on the results obtained, it can be concluded that the increase of trichloromethylsilane can increase hydrophobicity and opacity of glass. Besides, the addition of nanosilica also increases the hydrophobicity of the water repellent. Therefore, the methyltrihydroxysilane is really a potential material for water repellent regards to its hydrophobicity and contact angle, and especially it is best for applications that do not need transparency.

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