Hydrophobic Material Effect of Alkyl Chain Length on the Surface Roughness

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Hydrophobic Material: Effect of Alkyl Chain Length on the **Surface Roughness**

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Abstract: The clean technologies of self-cleaning surfaces are expanding rapidly. Highly hydrophobic coatings with strong adhesion, high durability, and dirt-free surfate have been prepared via sol-gel deposition of SiO2-TiO2-alkylsilane. The influence of the effects of the alkyl chain length of silane on surface roughness was investigated. This deposition involved a one-layer technique to produg the rough surfaces. The bimetal oxide of SiO2-TiO2 created a high level of surface roughness. As a result, the water contact angle the coatings increased with the increasing alkyl chain length of silane (up to C=8). However, the water contact angle decreased when the C=16 of alkylsilane was applied. It was predicted that the longer alkyl chain would cause to collapse. The higher hydrophobicity was produced by SiO2-TiO2-OTMS coatings with a water contact angle of about $140.67 \pm 1.23^{\circ}$. The effect of the dip-coating technique (one layer and layer-by-layer) on hydrophobicity was also discussed. The results showed that coatings produced by the one-layer technique had a higher contact angle than coatings made by the layer-by-layer technique. The coatings were stable under outdoor exposure and able to hinder dirt attachment to their surfaces.

Keywords: clean technologies; self-cleaning; hydrophobic; alkyl chain length; SiO2-TiO2-alkylsilane



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1. Introduction

Hydrophobic materials are widely used for self-cleaning surfaces. Self-cleaning is the ability of coatings to clean thei 14 rface by themselves. Hydrophobic coatings perform a self-cleaning action through the formation of spherical water droplets that readily roll away from the surface, carrying the dirt with them. The different mechanisms of hydrophobic self-cleaning were revealed on hydrophobic, highly hydrophobic, and superhydrophobic coatings [1]. In other words, the water contact angle greatly influences the performance and mechanism of self-cleaning properties.

The highest self-cleaning efficiency was observed on the superhydrophobic surface, which was prepared using TEOS, polydimethylsiloxane, and nanosilica. The dirt accumulated on the superhydrophobic surfaces at about 34.99% and decreased to 4.13% after the aning process. Air was trapped on the superhydrophobic surface [2]. This trapped air reduced the con 47 area between the water droplet and the surface. The water droplets easily rolled off the surface due to the low water adhesion properties of the surface. Therefore, no dirt remained on the surface [3].

29 ydrophobicity is influenced by surface energy and surface roughness. Based on the Young equation, the highest contact angle will be achieved with the lowest surface energy and highest surface roughness. Fluorosilane presents the lowest surface energy. Unfortunately, it is classified as a toxic compound [4,5]. Recently, researchers have been

considering the replacement of fluorosilane with alkylsilane. As we know, the surface energy of alkylsilane is higher than fluorosilane, therefore it must be modified with a rough surface to achieve high hydrophobicity. This roughness is achieved by etching, sol-gel, electrochemical deposition, chemical grafting, chemical vapor deposition, and nanoparticle deposition [6].

Superhydrophobic glass was successfully produced by the deposition of SiO₂ and alkylsilane [7–10]. More than one alkylsilane was needed to decrease the surface energy. Consequently, it created greater thickness and caused lower adhesion between the coatings and the glass substrate [11]. In other words, although superhydrophobic glass was achieved, 24 re were still limitations to the adhesion of coatings, as reported by Liu et al. [12]. In practical applications, the main criterion for the acceptable performance of coated materials is the bonding strength of the coating to the substrate. Some researchers have reported ways to overcome this problem, such as adding SiO₂ sol to increase the amount of the hydroxyl group, using SiO₂-TiO₂ composite, applying a dip coating method, and the sol-gel deposition technique [2,7,13,14].

For this research, we fabricated highly hydrophobic glass and enhanced the adhesion strength by coating the glass using SiO₂, TiO₂, and one alkylsilane via sol-gel deposition. The effects of long-chain alkylsilane on the hydrophobicity of coated glass have been investigated. Three alkylsilanes with different chain lengths were studied: methyltrimethoxysilane (MTMS, C=1), octyltrimethoxysilane (OTMS, C=8), and hexadecyltrimethoxysilane (HDTMS, C=16). Spataru and co-workers [15] reported that samples containing long hydrocarbon chains are highly hydrophobic. The increase in the hydrocarbon chain length contributed to higher non-polar properties in the C g groups. However, Tang and colleagues [16] stated that the short alkyl chain of silane exhibited a high water-contact angle. The surface coupling of the short alkyl chain of silane and the vertical polymerization (intermolecular silane coupling) created thick films with micro-nanoscale roughness. We also discuss the influence of dip-coating techniques (both layer-by-layer and one-layer). Our research also studied the self-cleaning performance of samples. Our results show that coated glass with SiO2-TiO2-OTMS displays the highest hydrophobicity. Interestingly, the as-prepared glass exhibits unique properties when a self-cleaning test is applied. The coated glass hinders the dirt's attachment to the surface; therefore, water is not required to clean the surface.

2. Materials and Methods

2.1. Materials

Tetraethylorthosilicate (1_{42})S, 99%) and titanium tetraisopropoxide (TTIP, 97%) as the SiO₂ and TiO₂ precursor, were purchased from Sigma Aldrich, St. Louis, MO, USA. Methyltrimethoxysilane (MTMS, 95%), octyltrimethoxysilane (OTMS, 96%), and hexadecyltrimethoxysilane (HDTMS, 85%) as the hydrophobic modifier were obtained from TCI Chemicals, Tokyo. Glacial acetic acid (100%) as acid catalyst was purchased from Merck, Rahway, NJ, USA. Absolute ethanol was purchased from JT Baker, Princeton, NJ, USA. All these materials were used as received without any further purification. Glass slides (38 \times 12 \times 1 mm) were used as a substrate.

2.2. Preparation of Acid-Catalyzed SiO₂-TiO₂-Alkylsilane Sol

SiO₂-TiO₂-MTMS sol was fabricated by mixing SiO₂, TiO₂, and MTMS sols. S₃₇, TiO₂, and MTMS sols were prepared in separate containers. First, 7.5 mmol of SiO₂ sol was prepared by mixing 1.67 mL of TEOS in 4 mL of ethanol. Then, 7.5 mmol of TiO₂ sol was made by mixing 2.22 mL of TTIP with 4 mL of ethanol. Then, 15 mmol of M₃₄IS sol was prepared by adding 2.1 mL of MTMS into 4 mL of ethanol. In all sols, the pH was adjusted to pH 2 with the addition of glacial acetic acid. Each sol was further stirred for 60 min at 70 °C. After that, the SiO₂ and Ti₃ sols were mixed and stirred continuously for 60 min at 70 °C. The MTMS sol was then added to the SiO₂-TiO₂ sol. The sol was then stirred and heated at 70 °C until the volume was 20 mL.

The effects of the SiO₂, TiO₂, and MTMS sols on hydrophobization were studied by varying the mol value. The various amounts of SiO₂, TiO₂, and alkylsilane were 3.75, 7.5, 15, and 30 mmol, respectively. While the mol of SiO₂ was varied, we kept the mols of TiO₂ and MTMS constant. The optimum mol of SiO₂ and the constant mol of MTMS were handled to investigate the influence of the amount of TiO₂. The variation in MTMS mol was studied using the optimum mols of SiO₂ and TiO₂.

The influence of the alkyl chain length of silane was investigated using SiO_2 - TiO_2 -MTMS, SiO_2 - TiO_2 -OTMS, and SiO_2 - TiO_2 -HDTMS sols. The preparation procedures of these sols were similar to previously described methods used in the preparation of SiO_2 - TiO_2 -MTMS.

2.3. Preparation of Coatings

The glass substrates were cleaned with ultrasonication in ethanol for 30 min. The cleaned glass was then immersed in the coating solutions, with a withdrawal speed of 3 cm/min. The one-layer coating technique was conducted using SiO₂, TiO₂, and alkylsilane, prepared in one vessel. Af 35 mmersion of the glass in the coating solution, the coated glass substrates were firstly dried at room temperature (33 °C) for 10 min and then at 70 °C for 30 min.

In the layer-by-layer deposition, the SiO_2 , TiO_2 , and alkylsilane sols were prepared separately. SiO_2 , TiO_2 , and alkylsilane were employed as the strong layers. Each layer was cured at room temperature (33 °C) for 10 min, and then followed at 70 °C for 30 min. The one-layer technique was formed as a one-time coating onto the substrates. Meanwhile, the layer-by-layer technique was applied in three layers, wherein SiO_2 , TiO_2 , and alkylsilane were deposited one by one. This means that the first, second, and third layers were SiO_2 , TiO_2 , and alkylsilane, respectively.

2.4. Characterization

The contact angle of the coated glasses was measured via ImageJ software (V.1.8.0, Bharti Airtel Ltd) using the drop analysis–drop snake method. The types of chemical bonds were identifie coating. Fourier transform infrared spectroscopy (Shimadzu IR-Tracer 100, Europe). The spect coating was recorded in the wavenumber range of 4000–400 cm⁻¹. The surface topography and roughness value of the samples were measured using atomic force microscopy (N8 Neos B 32 e, Herzogenrath, Germany) in the non-contact mode under ambient conditions. The morphology of the surfaces was studied using scanning electron microscopy (Carl Zeiss EVO MA 10, Oberkochen, Germany). The cross-cut adhesion test according to ASTM D3359 was employed to determine the adhesion quality of the coatings. The stability of coatings was studied by measuring the change in water contact angle under outdoor exposure for one month, with a relative humidity of between 38 and 76% and a temperature of between 23 and 35 °C.

2.5. Anti-Dirt Test

The performance of the samples' anti-dirt properties was evaluated using $CuCl_2.2H_2O$ as artificial dirt. The choice of $CuCl_2.2H_2O$ was adopted from previous research [17]. The coated glass was spiked with $CuCl_2.2H_2O$ and was then weighed (m_1) . The glass was then placed in an inclined position. Water was then dripped slowly onto the top side of the glass. After that, the glass was re-weighed (m_2) to determine the amount of $CuCl_2.2H_2O$ that was still left on the surface. The amount of $CuCl_2.2H_2O$ remaining was calculated using Equation 1. The less $CuCl_2.2H_2O$ there was on the surface, the better the self-cleaning properties of the glass. As a control, a self-cleaning test was also carried out on the uncoated glass.

The amount of remaining dirt on the surface (%) =
$$\frac{m_2}{m_1} \times 100\%$$
 (1)

3. Results and Discussion

3.1. Wetting Properties of Coatings with Various Compositions of SiO2 and TiO2

 ${
m TiO_2}$ plays a major role in the wettability of surfaces. The hydrophobic surfaces that were prepared using amorphous ${
m TiO_2}$ presented a stale water-contact angle. The ${
m TiO_2}$ phase of ${
m SiO_2}$ - ${
m TiO_2}$ -alkylsilane was investigated using X-ray diffraction (XRD) analysis. The XRD spectra of samples are depicted in Figure 1. All samples showed broad peaks, indicating that the sample had amorphous ${
m TiO_2}$. Under UV irradiation, amorphous ${
m TiO_2}$ did not demonstrate photocatalytic properties [16]. There were no hydroxyl groups that were released under UV irradiation. As we know, the hydroxyl groups have hydrophilic properties; therefore, this can decrease the contact angle of the coatings.

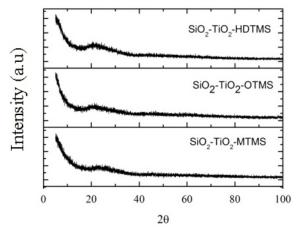


Figure 1. The XRD diffractogram of the samples.

Figure 2 shows the contact angle with respect to the SiO₂ and TiO₂ in the sol. The contact angle increased with increasing SiO2 and TiO2 content from 3.75 to 15 mmol. With SiO₂ and TiO₂ abo 4915 mmol, the water contact angle was decreased. These results were influenced by the surface roughness of the coatings. The roughness of the coatings, as measured using SEM, is displayed in Figure 3. Figure 3a-c displays the SEM images of samples using 7.5, 15, and 30 mmol of SiO₂. It can be seen that 15 mmol of SiO₂ presented a rougher surface than the others. This is because the clustering of SiO2 on the surfaces created rougher surfaces. With SiO2 above 15 mmol, the surface morphology of the coating became smooth. The high content of SiO₂ tended to fill the surface holes and create smooth surfaces. A similar trend of topography was also observed for 7.5, 15, and 30 mmol of TiO₂ (Figure 3d-f). Comparing the topography of the coatings with various compositions of SiO₂ and TiO₂, the roughest surface was obtained from the deposition of 15 mmol of TiO₂. The agglometrion of particles was clearly obvious. This particle agglomeration resulted in irregular surfaces. According to 522 data regarding 43 ater contact angle and the SEM images, it can be concluded that the 22 ugh 23 the surface is, the higher the hydrophobicity. Table 1 shows the data regarding water 23 tact angle and the roughness value of the samples, which were measured by AFM.

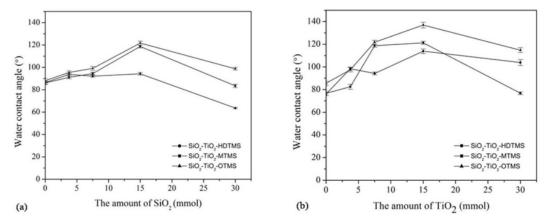


Figure 2. Water contact angle of SiO_2 - TiO_2 -alkylsilane coatings prepared with various compositions of (**a**) SiO_2 (x mmol SiO_2 , 7.5 mmol TiO_2 , and 15 mmol alkylsilane) and (**b**) TiO_2 (15 mmol SiO_2 , x mmol TiO_2 , and 15 mmol alkylsilane).

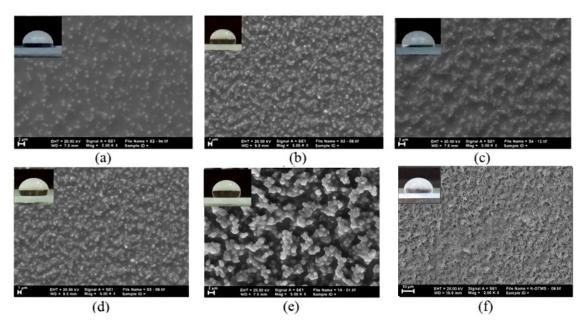


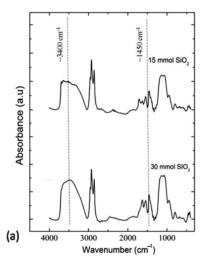
Figure 3. The SEM images of SiO_2 -TiO₂-OTMS coatings prepared with (a) 7.5, (b) 15, and (c) 30 mmol of SiO_2 (x mmol SiO_2 , 7.5 mmol TiO_2 , and 15 mmol OTMS), (d) 7.5, (e) 15, and (f) 30 mmol of TiO_2 (15 mmol SiO_2 , x mmol TiO_2 , 15 mmol OTMS), respectively.

The decrease in water contact angle in over 15 mmol of SiO_2 and TiO_2 was also attributed to the increase in the amounts of the hydroxyl groups on the surfaces. The presence of hydroxyl groups areas of O-H (~3400 cm^{-1}) and C-H (~3400 cm^{-1}) vibration in 15 and 30 mmol of SiO_2 and TiO_2 , based on the FTIR data, to quantify the hydroxyl groups on the surface (Figure 4). It was found that 15 mmol of SiO_2 and TiO_2 had higher A $\frac{3400 \text{ cm}^{-1}}{1450 \text{ cm}^{-1}}$ values than 15 mmol of SiO_2 and TiO_2 . It means that 15 mmol of SiO_2 and TiO_2 had higher hydroxyl groups than 15 mmol of SiO_2 and TiO_2 . The abundance of hydroxyl groups on

the surface caused an increase in its hydrophilicity. Table 2 shows the ratio of peak areas of O-H to C-H vibration from the FTIR spectra of SiO_2 - TiO_2 -OTMS samples.

Table 1. The correlation of water contact angle and roughness value of SiO_2 - TiO_2 -OTMS coatings prepared with reprious SiO_2 and TiO_2 values.

Sample	x (mmol)	Water Contact Angle (°)	Roughness Value (nm)
x SiO ₂ , 7.5 mmol TiO ₂ , 15 mmol OTMS	7.5 15 30	99.09 ± 1.73 121.75 ± 1.71 98.79 ± 1.21	11.2 157 12.9
15 mmol SiO ₂ , x TiO ₂ , 15 mmol OTMS	7.5 15 30	$\begin{array}{c} 121.75 \pm 1.71 \\ 136.92 \pm 2.45 \\ 114.77 \pm 2.15 \end{array}$	163 235 87



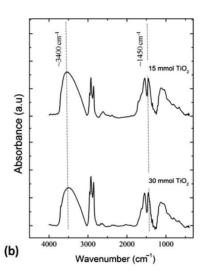


Figure 4. The FTIR images of SiO₂-TiO₂-OTMS coatings prepared with various compositions of (a) SiO₂ and (b) TiO₂.

Table 2. The ratio of peak areas of O-H to C-H vibration at 3400 and 1450 cm⁻¹ from FTIR spectra of SiO₂-TiO₂-OTMS samples with various compositions of SiO₂ and TiO₂.

Sol	Composition	The Ratio of Pe	he Ratio of Peak Areas (A) at-	
301	(mmol)	3400 cm ⁻¹	1450 cm ⁻¹	A 3400 cm ⁻¹ 1450 cm ⁻¹
SiO ₂	15	71.32	7.074	10.082
	30	42.50	4.12	10.315
TiO ₂	15	64.12	12.97	4.94
	30	100.47	15.85	6.33

In order to study the effect of SiO₂ and TiO₂ on hydrophobicity, measurements such as the water contact angle test, AFM analysis, and cross-cut adhesion test were employed. Table 3 reveals the water contact angle of coated glass using SiO₂-MTMS, TiO₂-MTMS, and 53)₂-TiO₂-MTMS. It was observed that SiO₂-MTMS, TiO₂-MTMS, and SiO₂-TiO₂-MTMS resulted in a water contact angle of about 63.73 \pm 1.58°, 80.03 \pm 1.45°, and 126.18 \pm 1.86°. The use of SiO₂-TiO₂ produced higher hydrophobicity than others.

Table 3. The influence of SiO₂, TiO₂, and SiO₂-TiO₂ on the hydrophobicity of coatings.

	Composition (mmol)		— Water Contact Angle	
SiO ₂	TiO ₂	MTMS	— Water Contact Angle	
30	-	30	63.73 ± 1.58°	
-	30	30	$80.03 \pm 1.45^{\circ}$	
15	15	30	$126.18 \pm 1.86^{\circ}$	

To address these concerns, we analyzed the topography of SiO₂-MTMS, TiO₂-MTMS, and SiO₂-TiO₂-MTMS using AFM as shown in Figure 5. As a result, the topography surface of SiO₂-TiO₂-MTMS was rougher than SiO₂-MTMS and TiO₂-MTMS. The roughness values of SiO₂-MTMS, TiO₂-MTMS, and SiO₂-TiO₂-MTMS were 4.95, 18.60, and 173 nm, respectively. The average particle sizes of SiO₂-MTMS and TiO₂-MTMS were 0.472 and 0.175 μm , respectively. The previous research stated that SiO₂ resulted in higher particle size than TiO₂ under similar conditions [18]. It can be assumed that the difference in particle size between SiO₂ and TiO₂ led to an increase in the hierarchical morphology.

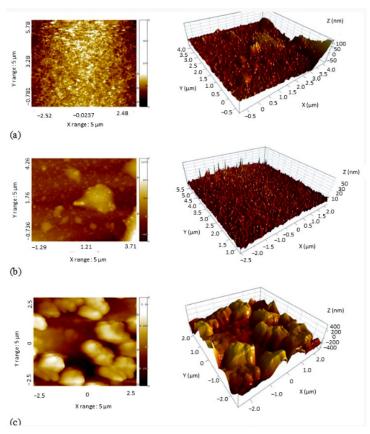


Figure 5. The AFM images of (a) SiO₂-MTMS, (b) TiO₂-MTMS, and (c) SiO₂-TiO₂-MTMS coatings.

 SiO_2 - TiO_2 also improves the adhesion of coatings. The cross-cut adhesion test was conducted with the SiO_2 -MTMS, TiO_2 -MTMS, and SiO_2 - TiO_2 -MTMS-coated glass. According to ASTM D3359, it was observed that the SiO_2 - TiO_2 -MTMS had the highest adhesion of the coating, rated as 4B. Ramirez-Garcia and colleagues also reported that the use of SiO_2 - TiO_2 increased the adhesion of coatings [12].

3.2. The Influence of Composition and the Alkyl Chain Length of Silane on Hydrophobicity

Figure 6 displays the water contact angle of coated glass with various compositions of alkylsilane. Both ${\rm SiO_2\text{-}TiO_2\text{-}MTMS}$ and ${\rm SiO_2\text{-}TiO_2\text{-}OTMS}$ show that hydrophobicity increases with an increase in the amount of alkylsilane from 0 to 30 mmol. The decrease in the water contact angle was obtaine 00 60 mmol of MTMS and OTMS. Moreover, the ${\rm SiO_2\text{-}TiO_2\text{-}HDTMS}$ coatings resulted in an increase in water-contact angle with increasing HDTMS content, from 0 to 15 mmol. In 30 mmol of HDTMS, the water contact angle was reduced. Unfortunately, the observation could not be completed at up to 60 mmol of HDTMS because the sol then changed to a gel. Moreover, the highest contact angle of $140.67 \pm 1.23^\circ$ was achieved by those coatings with 15:15:30 mmol of SiO₂:TiO₂:OTMS.

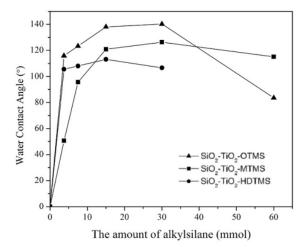


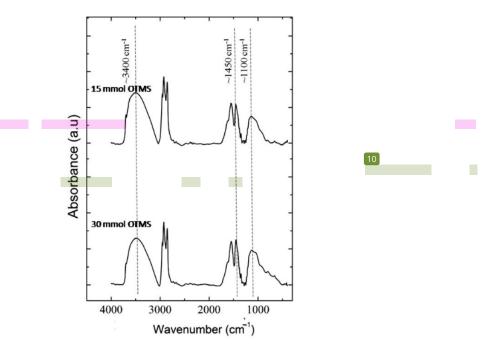
Figure 6. The water contact angle of SiO_2 - TiO_2 -alkylsilane coatings prepared with various compositions of silane.

The increase in hydrophobicity might be due to the replacement of the polar –OH groups by non-polar –CH₃ groups of silane. The FTIR spectra proved this replacement, based on the data of the peak area ratios of O-H to Si-O-Si vibration and C-H to Si-O-Si vibration (Figure 7 and Table 4). There was a decrease in the peak area ratios of O-H to Si-O-Si vibration, which contributed to the decrease in –OH group abundance on the surface. The data also presented an increase in the peak area ratio of C-H to Si-O-Si vibration, which indicated that the number of –CH₃ groups on the surface had increased.

Table 4. The ratio of peak areas of O-H to Si-O-Si at 3400 and 1100 cm⁻¹ and the C-H to Si-O-Si vibration at 1450 and 1100 cm⁻¹ from the FTIR spectra of SiO₂-TiO₂-OTMS samples with various compositions of OTMS.

Composition	The Ratio of Peak Areas (A) at-		A 3400 cm ⁻¹	A 1450 cm ⁻¹	
(mmol)	$3400 \ {\rm cm}^{-1}$	1450 cm^{-1}	$1100 \mathrm{cm}^{-1}$	1100 cm ⁻¹	1100 cm ⁻¹
15	108.1	18.59	32.29	3.35	0.57
30	93.6	18.61	40.54	2.31	0.46

The SEM images also revealed that the rougher surfaces were formed by the higher content of alkylsilane (Figure 8). The dispersion of alkylsilane created holes on the surface and tended to produce a hierarchical surface. However, the surface roughness decreased when a larger amount of alkylsilane was applied. The molecules of silane, as predicted, 19ed the grooves and produced smooth surfaces; therefore, the coatings presented a low contact angle.



9 of 16

Figure 7. The FTIR images of SiO_2 - TiO_2 -OTMS coatings, prepared with various compositions of OTMS

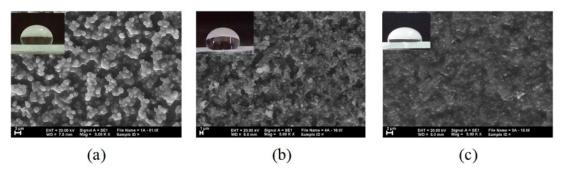


Figure 8. The SEM images of SiO₂-TiO₂-OTMS coatings prepared with (a) 15, (b) 30, and (c) 60 mmol of OTMS.

The main difference between MTMS, OTMS, and HDTMS is the alkyl chain length of silane. The alkyl chain length of MTMS, OTMS, and HDTMS are 1, 8, and 16, respectively. The measured water contact angle of SiO_2 - TiO_2 -MTMS, SiO_2 - TiO_2 -OTMS, and SiO_2 - TiO_2 -HDTMS coated glass under similar conditions is also depicted in Figure 9. It was clear that increasing the alkyl chain length up to C=8 increased the water contact angle, due to the non-polar contribution from alkylsilane. The contact angle value increased with an increase in the alkyl chain length. Coating with long alkyl-chain silane significantly reduced the surface energy of the glass, which was also favorable for enhancing the water-repellent effect.

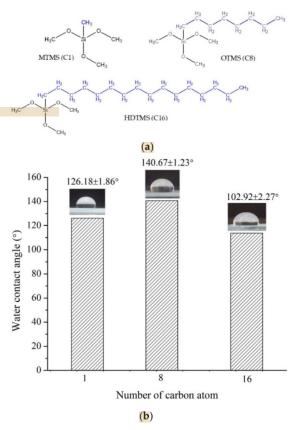


Figure 9. (a) The molecular structure of MTMS (C1), OTMS (C8), HDTMS (C16), and (b) water contact angles, measured on SiO_2 - TiO_2 -alkylsilane coated glass samples.

However, the water contact angle of C=16 showed the opposite trend. The measured contact angle was decreased. According to the surface energy, HDTMS (C16) should have lower surface energy than MTMS (C1) and OTMS (C8); therefore, HDTMS should present a higher contact angle than other samples. In fact, coating the glass samples with SiO_2 - TiO_2 -HDTMS resulted in the lowest contact angle.

To study the effect of alkyl chain-length silane on hydrophobicity, we characterized the topography of coated glass samples using SEM and AFM. The SEM images of SiO₂-TiO₂-MTMS, SiO₂-TiO₂-OTMS, and SiO₂-TiO₂-HDTMS coated glass samples are shown in Figure 10. The SiO₂-TiO₂-HDTMS presented a lower surface roughness than SiO₂-TiO₂-MTMS and SiO₂-TiO₂-OTMS. The smooth surface of the SiO₂-TiO₂-HDTMS proved that the long chains of HDTMS did not align vertically on the surface and instead formed collapsed molecules.

3.3. The Influence of Surface Roughness on Hydrophobicity

The profile of the surface roughness was displayed in Figure 11. It showed the AFM images of SiO₂-TiO₂-MTMS, SiO₂-TiO₂-OTMS, and SiO₂-TiO₂-HDTMS. The samples showed that the root mean square (RMS) values were 188 nm for SiO₂-TiO₂-MTMS, 291 nm for SiO₂-TiO₂-OTMS, and 29.8 nm for SiO₂-TiO₂-HDTMS, respectively. An analysis of both showed that the SiO₂-TiO₂-HDTMS evinced the smoothest surfaces, while SiO₂-TiO₂-OTMS presented the roughest surfaces. This data supported the results and analysis of SEM images.

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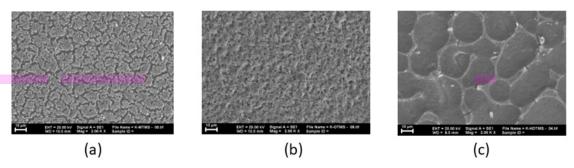


Figure 10. The SEM images of (a) SiO₂-TiO₂-MTMS, (b) SiO₂-TiO₂-OTMS, and (c) SiO₂-TiO₂-HDTMS.

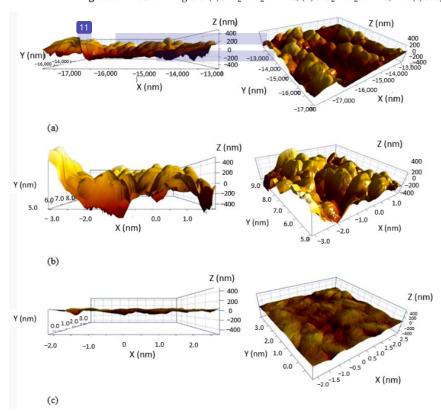


Figure 11. The AFM images of (a) SiO_2 - TiO_2 -MTMS, (b) SiO_2 - TiO_2 -OTMS, and (c) SiO_2 - TiO_2 -HDTMS coatings.

On the rough surfaces, there was trapped air that filled the grooves on the surface. When the water dropped onto the surface, entrapped air gave an upward thrust, resulting in an adhesion force toward water droplets. It is not easy for the water to penetrate the solid surface. It will rest on top of the surface and minimize the interaction between the water and the solid. Finally, a hydrophobic surface is generated. The larger area of entrapped air, and the lower the interaction of the water–solid, the higher the hydrophobicity. Consequently, the portion of air trapped in the solid surface is the main factor in controlling hydrophobicity. Figure 12 illustrates the correlation between surface roughness and hydrophobicity.

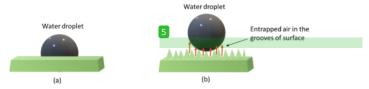


Figure 12. A schematic illustration of a water droplet on (a) smooth and (b) rough surfaces.

AFM images can also identify and determine the orientation of molecules on the surface, which influences the topography of the surface. SiO_2 - TiO_2 -MTMS, SiO_2 - TiO_2 -OTMS, and SiO_2 - TiO_2 -HDTMS films had surface heights of about 100-300, 100-400, and 0-50 nm, respectively. The SiO_2 - TiO_2 -MTMS and SiO_2 - TiO_2 -OTMS coatings formed self-assembled molecules because the longer the alkyl chain, the greater the height of the coating on the surface. In contrast to SiO_2 - TiO_2 -MTMS and SiO_2 - TiO_2 -OTMS, SiO_2 - TiO_2 -HDTMS demonstrated a low height of surface. It was predicted that HDTMS with a long alkyl chain would create self-assembly disorder. We assumed that most of the molecules formed a collapsed structure on the surfaces. Molecules tended to form a horizontal orientation on the surface. The prediction of the molecule conformation of coatings is displayed in Figure 13. These data were in line with previous research, which stated that collapsed molecules generated smooth surfaces [16].

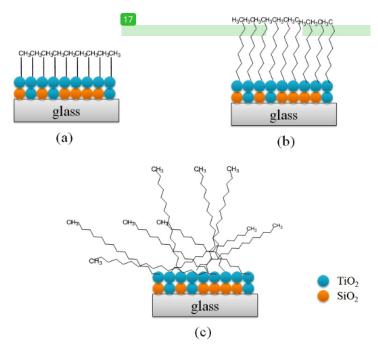


Figure 13. The prediction of molecule conformation of (a) SiO_2 - TiO_2 -MTMS, (b) SiO_2 - TiO_2 -OTMS, and (c) SiO_2 - TiO_2 -HDTMS-coated glass.

In the collapsed next cules, the water-surface interaction of CH₂ groups was greater than with CH₃ groups when the water droplets were sitting on the surface [19,20]. As we know, CH₂ groups create higher surface energy than CH₃ groups; therefore, the collapsed molecules tended to produce a low contact angle.

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3.4. The Influence of Coating Technique on Hydrophobic Coatings

Figure 14 shows the influence of the coating technique on the hydrophobicity and surface roughness of coated glass samples. Coatings made by the one-layer technique had a higher contact angle than coatings created by the layer-by-layer technique. This can be attributed to the difference in surface roughness. The higher surface roughness was observed in the one-layer technique. The rougher the surface, the higher the hydrophobicity. In contrast, the layer-by-layer technique created smooth surfaces. The loss of surface roughness could have occurred when the thick coating covered the metal oxide layers [21].

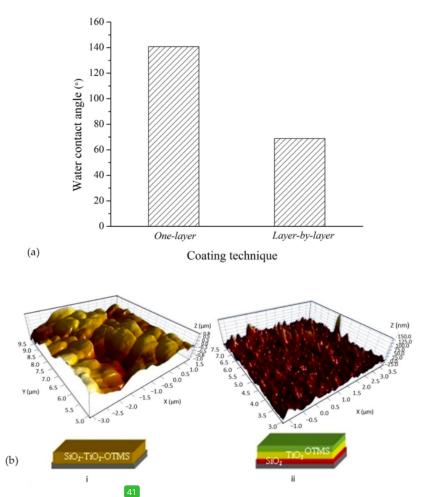


Figure 14. (a) The correlation between water contact angle and the coating technique of SiO_2 , TiO_2 , and OTMS-coated glass. (b) The AFM images of SiO_2 , TiO_2 , and OTMS-coated glass were prepared using (i) one layer and (ii) layer-by-layer coating techniques.

3.5. Stability of Coatings

Figure 15 displays the stability of coatings undergoing outdoor exposure for four weeks. The hydrophobicity of SiO₂-TiO₂-MTMS and SiO₂-TiO₂-HDTMS coatings gradually degraded during outdoor exposure. In contrast, the water-repellent capability of the SiO₂-TiO₂-OTMS coating was stable for four weeks. The decrease in contact angle was probably due to the absorption of moisture from the atmosphere by the polar –OH bonds

in the surfaces [22]. A similar result was also obtained in our previous research [11]. The stability of SiO₂-TiO₂-OTMS was predicted because of the contribution made by its surface roughness. The high surface roughness was expected to make it difficult for dirt to adhere.

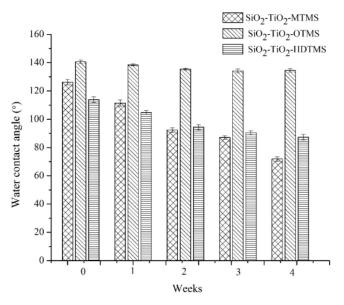


Figure 15. The change in the water contact angle of coatings undergoing outdoor exposure for four weeks.

3.6. Anti-Dirt Performance of Coatings

Up to now, there has been no standard procedure for investigating the self-cleaning performance of coatings [2]. Figure 16 shows the difference in the behavior of uncoated glass and coated glass after dirt deposition on their surfaces. On the uncoated glass, a great deal of dirt accumulated on the surface. In contrast, there was no dirt adhering to the highly hydrophobic surface. The very rough surface was predicted to be able to prevent dirt attachment to the coating.

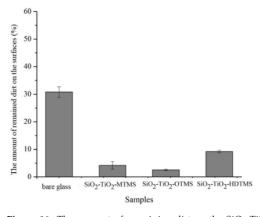


Figure 16. The amount of remaining dirt on the SiO₂-TiO₂-OTMS coated glass surface after the self-cleaning test.

4. Conclusions

A highly hydrophobic, anti-dirt, and durable coating was prepared using SiO₂-TiO₂-alkylsilane through sol-gel depos 15 n and the one-layer coating technique. The use of SiO₂ and TiO₂ helped to enhance the surface roughness and adhesion st 15 gth of the coatings. The longer the alkyl chain length of silane (up to C=8), the higher the hydrophobicity of the coatings. However, the water contact angle decreased when the C=16 formulation of alkylsilane was applied. It was predicted that the surfaces were then composed of disordered molecules. Interestingly, the as-prepared samples demonstrated the anti-dirt accumulation performance on the surfaces, so that no water was needed to clean the surfaces. Further research will focus on the engineering of coatings to maintain the transparency of glass. Based on its high hydrophobicity, durability, and excellent anti-dirt properties, this coating shows promise in many applications.

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