

Article

Super-Amphiphobic Coating System Incorporating Functionalized Nano-Al₂O₃ in Polyvinylidene Fluoride (PVDF) with Enhanced Corrosion Resistance

Nadiah Ghazali^{1,*}, Wan Jeffrey Basirun², Azmi Mohammed Nor³ and Mohd Rafie Johan^{4,*}

- ¹ Mechanical Engineering Department, Faculty of Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia
- ² Chemistry Department, Faculty of Science, University of Malaya, 50603 Kuala Lumpur, Malaysia; jeff@um.edu.my
- ³ Petronas Research Sdn. Bhd. Jalan Ayer Itam, Kawasan Institusi Bangi, 43000 Bandar Baru Bangi, Selangor, Malaysia; azminr@petronas.com
- ⁴ Nanotechnology and Catalysis Research Center (NANOCAT), University of Malaya, 50603 Kuala Lumpur, Malaysia
- * Correspondence: diyaghaz@yahoo.com (N.G.); mrafiej@um.edu.my (M.R.J.)

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Abstract: Understanding the corrosion inhibition behavior of super-amphiphobic coating is important to ensure practicability in the real application. 2 layers system of super-amphiphobic coating was successfully developed using functionalized nano- Al_2O_3 incorporated in polyvinylidene fluoride (PVDF). This study investigates the effect of different amount of functionalizing agent on the coating's repellency and its relationship toward the corrosion inhibition behavior. We found that a higher amount of fluoroalkylsilane (FAS) led to a decreased in repellency of both water and oil. Electrochemical impedance spectroscopy (EIS) analysis suggests that the synergetic effect between super-hydrophobicity, longer diffusion path, and barrier effect; enhanced the corrosion resistance. Although the coatings demonstrate similar behavior, the most superhydrophobic/amphiphobic coating C1 offers the highest corrosion protection.

Keywords: superhydrophobic; amphiphobic; fluoroalkylsilane; alumina; corrosion protection; EIS

1. Introduction

Superhydrophobic coating has garnered much interest due to its wide applications in science and engineering. Some of the recent applications of superhydrophobic coating are self-cleaning, anti-icing, and anti-corrosion have been reported in recent years [1–6]. Having a dual property surface called superamphiphobic further enhances the property of the coating. A combination of water- and oil-repelling surfaces could increase the efficiency of superhydrophobic coating, which is easily stained by oil. In certain applications, such as in pipelines, the amphiphobic surface can also increase flowability.

A superamphiphobic coating repels oil by fine-tuning the surface characteristic. One of the challenges to form superamphiphobic surfaces is that the lower surface tension of oils is similar to those of low-energy materials [7]. In this study, we used a fluoroalkylsilane (FAS) molecule, 1H,1H,2H,2H-perfluorodecyltriethoxysilane as the low energy material. The FAS possesses a long chain of fluorinated carbon atom that lowers the surface energy and is used as a functionalization agent for the oxide nanoparticles. The amount of FAS was also varied to observe the effect on the wetting properties.



In addition to the low surface energy of the material, surface roughness and re-entrant structure are essential to achieve amphiphobicity. Surface roughness is associated with hydrophobicity and can be attained by introducing solid materials such as nickel [8], graphene [9,10], cerium [11], and metal oxides such as TiO_2 , SiO_2 , and Al_2O_3 . Although SiO_2 is the more common material [12–15], Al_2O_3 has also been used since it is harder compared to SiO_2 and mostly used to improve the scratch and abrasion resistance [16].

The re-entrant surface is a geometry where the surface asperities create an overhang or "liquid sagging" [17]. Example of re-entrant phenomena is the surface of the gills of a standing mushroom, inverse trapezoidal, and the bottom half of a sphere [13]. When a liquid is subjected to the surface, the surface tension is pointing upward and able to support the liquid-vapor interface. Therefore, the liquid does not fully wet the surface [17].

Lina Ejenstam et al. [18] investigated the corrosion properties of hydrophobic multilayer nano-composite coating using a thin composite polyester acrylate (PEA)– TiO_2 –hexamethyl disiloxane (HMDSO) coating system. The study shows that it required all three layers to reach and maintain the desired corrosion protective property. In this study, we proposed a two-layer coating system using functionalized alumina and polyvinylidene fluoride (PVDF). Due to the very low energy functionalization, the coating is expected to exhibit an amphiphobic property. Furthermore, by varying the functionalization parameter, a different degree of repellency is anticipated. Therefore, the influence of hydrophobicity towards corrosion inhabitation property can be investigated. It is crucial to understand the protection mechanism of such coating to fine-tune and enhance the inhabitation performance. However, there is a lack of detailed information that discusses the corrosion behavior of this type of coating. Therefore, this work presents a comprehensive study of the anti-corrosion performance of nano-sized alumina functionalized with FAS incorporated into PVDF coating.

2. Materials and Methods

2.1. Materials

Commercially available Al₂O₃ nano-powders supplied by Sigma Aldrich (St. Louis, MO, USA), polyvinylidene fluoride (PVDF) powders supplied by Sigma Aldrich (Lyon, France), and 1H,1H,2H,2H-perfluorodecyltriethoxysilane (FAS) was supplied by Sigma Aldrich (Bangalore, India). N,N-dimethylformamide (DMF) and Toluene were purchased from R&M Chemicals (Essex, UK). Absolute alcohol was purchased from VWR Chemicals (Fontenay-sous-Bois Cedex, France). All compounds and chemicals were used without further purification.

2.2. Experimental Procedure

In this study, functionalized alumina was prepared by dispersing 0.5 g nano-Al₂O₃ powder with primary particle size of 13 nm in 20 mL toluene for 30 min using ultrasonic bath. It was then stirred, followed by the dropwise addition of 0.1 mL FAS. The solution was stirred overnight before it was dried in an oven at 60 °C for 2 h. The functionalized Al₂O₃ (fn-Al₂O₃) powder was scrapped off the petri dish and kept in a container for further processing. The fn-Al₂O₃ powder was denoted as 0.1 fn-Al₂O₃. Subsequently, the processes were repeated with different FAS amounts (0.2, 0.3, 0.4, 0.5 mL).

The design of the coating consists of a top and bottom layer. The base layer was prepared by dissolving 1 g polyvinylidene fluoride (PVDF) in 10 mL dimethylformamide (DMF). The solution was stirred at 500 rpm while heated at 100 °C for 15 min. The viscous liquid was then casted onto pre-treated steel and cured in a pre-heated oven at 155 °C for 2 h.

Once the base coat was ready, 1 g of PVDF and 0.1 g 0.1 fn-Al₂O₃ were dispersed in 10 mL absolute alcohol for 2 h followed by ultrasonic dispersion for 30 min. The dispersion was sprayed on top of the base coat and heated in an oven at 160 °C for 2 h to form the top layer. The processes were repeated with different fn-Al₂O₃ parameters including pristine Al₂O₃ as reference sample (i.e., 0.0, 0.2, 0.3, 0.4,

0.5 fn-Al₂O₃). Subsequently, the sample was denoted as C0, C1, C2, C3, C4, and C5. The experimental procedure is summarized in Figure 1.



Repeat step 2.2 for other parameters

Figure 1. Illustration of the experimental procedure in this study starting from the functionalization process to the assembly of the bi-layer coating.

2.3. Characterization

To investigate the surface properties, water and n-hexadecane wetting angles were measured by DataPhysics OCA 20 Instruments GmbH (Filderstadt, Germany) contact angle instrument. The contact angle hysteresis was also measured to determine the water-rolling ability. The software (version 2.0) was put on the hysteresis measurement mode and the advancing-receding contact angles were measured. The difference between the advancing and receding contact angle yields hysteresis. The coating thickness of the dry films was measured using Elcometer 456 Coating Thickness Gauge (Manchester, UK). The morphological study was performed using field emission scanning electron microscopy (FESEM, Zeiss Auriga, Jena, Germany) with different magnifications while the bonding characteristics were analyzed using Fourier transformed infrared (FTIR, Perkin Elmer, Waltham, MA, USA) spectroscopy. The surfaces of the samples after the 30-day immersion were analyzed using an optical microscope (free from Meiji Optical Microscope (Saitama, Japan), model MT5300H/LBC.

2.4. Electrochemical Corrosion Measurements

Electrochemical impedance spectroscopy (EIS) measurement was conducted using Autolab PGSTAT302N potentiostat/galvanostat (Metrohm Autolab, Utrecht, The Netherlands) to investigate the corrosion behaviour and corrosion rate. The measurement was performed in 3.5% NaCl solution using a conventional three-electrode system. The EIS was performed between 100 kHz and 10 mHz with an amplitude potential of 10 mV around the open circuit potential (OCP). The samples were immersed into the solution 24 h before the start of the measurement to ensure that the coatings were saturated and stabilized. The OCP and EIS measurements were conducted for 30 days with a one-day interval. The polarization measurement (Tafel plot) was performed at the end of measurement, on the 30th day of immersion.

3. Results and Discussions

3.1. FTIR Analysis of Functionalized Al₂O₃

Figure 2 shows the FTIR spectra of pristine and functionalized Al_2O_3 (fn- Al_2O_3) with different amounts of FAS. The characteristic bands within 821 and 527 cm⁻¹ are attributed to pristine Al_2O_3 . The presence of alkylsilane characteristic bands between 1300 and 900 cm⁻¹ confirms the successful functionalization of the nano alumina with FAS. The prominent bands at 1204 and 1145 cm⁻¹ corresponds to the specific vibration bands of the perfluorinated chains group. The intensity of the band increases with the FAS amount is in agreement with previous reports [19,20].



Figure 2. FT-IR spectra of a pristine nano- Al_2O_3 (**a**) and functionalized alumina with different fluoroalkylsilane (FAS) values; (**b**) 0.1, (**c**) 0.2, (**d**) 0.3, (**e**) 0.4, and (**f**) 0.5 mL. The dotted lines show two prominent perfluorinated vibration bands.

The functionalization of Al₂O₃ occurs with the replacement of the hydroxyl groups on the metal oxide surface with different organofunctional groups as presented in Figure 3. These organofunctional groups are covalently bonded to the metal oxide surface once the condensation reaction is completed [19]. The functionalization lowers the surface energy leading to hydrophobicity, hence we varied the amount and investigated the effect on the hydrophobicity, as well as anti-corrosion performance of the coating.



Figure 3. The mechanism of Al_2O_3 surface functionalization where condensation reaction between Al_2O_3 and FAS yields functionalized Al_2O_3 . Adapted with permission from [19]; Copyright 2013 Elsevier.

3.2. Contact Angle Analysis

The contact angle (CA) of the coating was measured using a contact angle instrument with a 10 μ L dosing volume. It is a common practice to use 5 μ L dosing volume, however the small droplet would just roll off the surface, hence the larger volume was required for the droplet to stay on the surface. The CA is summarized in Table 1 and represents the mean of five measurements. The increase from 87.5° (PVDF base coat) to 125.2° (unfunctionalized Al₂O₃, C0) shows that roughness gives better hydrophobic property. Functionalization of Al₂O₃ yields higher water contact angle (WCA). The CA values indicate that the coatings were water repellent, and the highest value is 157.22° for coating C1 with 0.1 mL FAS. Coatings C1, C2, and C3 are superhydrophobic, however the WCA decreases with higher amount of FAS. Video of the superhydrophobicity is included in the electronic supplementary information (ESI) file (Video S1).

Table 1. Contact angle analysis for polyvinylidene fluoride (PVDF) base coat and different coating samples with different functionalized Al_2O_3 parameter.

Contact Angle (°)	PVDF Base	C0	C1	C2	C3	C4	C5
Water. WCA	87.5 ± 1.8	125.2 ± 0.4	157.2 ± 2.6	153.6 ± 2.9	152.0 ± 1.3	150.0 ± 1.5	146.4 ± 1.6
WCA Hysteresis	-	21.0	3.7	3.1	2.0	10.3	9.8
n-Hexadecane, HCA	46.1 ± 1.6	-	149.2 ± 1.4	133.5 ± 2.4	115.8 ± 1.6	98.9 ± 1.8	83.0 ± 1.4

Superhydrophobicity is characterized by a contact angle equal or more than 150° with a low contact angle hysteresis (<10°), while the contact angle hysteresis is interpreted as the droplet adhesion to the surface. A stronger droplet adherence to the surface is due to a higher hysteresis value. To further define the super-hydrophobic state, the advancing and receding CA was also measured to obtain the hysteresis value.

In this study, we found that a small amount of FAS was enough to produce a very low hysteresis effect with superior rollability properties. The hysteresis value increases with the amount of FAS, with greater water adherence to the coated surface. The hysteresis values for the first three parameters are 3.67°, 3.07°, and 2.00°, respectively. By taking into consideration both the WCA and hysteresis results, super-hydrophobicity was achieved with a maximum of 0.3 mL FAS (coating C3) before the effect becomes negligible.

To further assess the quality of the coating, the coating behavior towards oil was investigated using n-hexadecane. Figure 4 shows the repellent behavior of coating C1 and C5. The trend is similar

to water where a lower amount of FAS results in a higher wetting angle. The highest average repellency is 149.17° while the lowest is 83.04°, which suggests that the coating is also oleophobic.



Figure 4. Water contact angle (WCA) for sample (**a**) C1 and (**b**) C5, and n-hexadecane contact angle for sample (**c**) C1 and (**d**) C5.

The two different factors that contribute to the formation of amphiphobic surface are the surface chemistry and surface roughness. The functionalization of the Al_2O_3 surface with long chains of fluorinated carbon atoms changes the surface chemistry of Al_2O_3 . The chains dangle from the Al_2O_3 surface and consequently lowers the surface energy [21]. The lower surface energy is characterized by a significant increase in the wetting angle compared to a non-fluorinated sample. FTIR analysis shows that the increase of FAS concentration gives higher intensity bands, but the repellent behavior towards both water and n-hexadecane was also decreased. Wankhede et al. [22] suggested that the decrease in repellency at higher concentration of FAS could be attributed to the surface roughness. To further investigate this, we performed FE-SEM imaging, as discussed in the next section.

3.3. FE-SEM Analysis

The FE-SEM image in Figure 5 shows two different magnifications of the coating surface with respect to the FAS amount. From the micrographs, similar macro-scale bump morphology can be seen for all samples. Higher magnification reveals that the Al₂O₃ nanoparticles are distributed on top of the bumps creating a hierarchical structure. This observation is most prominent in coating C1 and becomes negligible with higher amounts of FAS.

When liquid is subjected to a hierarchical structure, it creates a composite of solid-liquid-air interface between the droplet and the coating surface. This effect is represented by the Cassie-Baxter model [23], which describes the superhydrophobic phenomena. The hierarchical structure also could lead to the formation of re-entrant surfaces at the bottom half of Al₂O₃ spheres, resulting in oleophobicity [13]. When the structure is no longer hierarchical, it becomes a Wenzel wetting state instead and the surface becomes less hydrophobic.

The combined effect of the surface structure and low surface energy renders the coating super-hydrophobic and oleophobic. The surface becomes smoother with the increase of FAS amount, due to Al_2O_3 agglomeration, which subsequently lowers the contact angle. Although it is no longer hierarchical, the surface energy is low enough to repel water and hexadecane with considerable CA value, as discussed in the previous section [24].



Figure 5. FE-SEM micrograph of coating surface with different magnification with respect to FAS amount (**a**) C1, (**b**) C2, (**c**) C3, (**d**) C4, and (**e**) C5. The morphology shows micro-bumps, which contribute to the roughness while C1 and C2 exhibit hierarchical structure.

3.4. Corrosion Protection Properties

The thickness of the coatings is similar, and the average dry film thickness is presented in Table 2. The thickness of the coatings must be around the same value, in order to have unbiased and comparable results of the corrosion protection properties. The results of EIS and Tafel measurements are discussed in the following sections.

Table 2. Dry film thickness of the different coating sample. The value presented is the average of 10 measurements.

Parameter	Dry Film Thickness (µm)	Standard Deviation (µm)		
C1	64.7	±9.0		
C2	68.1	±9.9		
C3	64.5	±8.9		
C4	65.3	±10.6		
C5	67.1	± 8.7		

3.4.1. EIS Analysis of PVDF Base Coat

The EIS behavior of PVDF base coat for selected days is depicted in Figure 6. The data were fitted to the equivalent circuit model and is included in the electronic supplementary information (ESI) file (Tables S1–S6). The first Nyquist plot shows a large semi-circle, which is usually associated with good barrier properties. However, closer inspection reveals the presence of a smaller semicircle at higher frequencies. This is barely noticeable probably due to the smaller electrochemical reaction at the interface during immersion. This leads to the difficulty to separate the time relaxation between the coating's physical impedance and the electrochemical reaction impedance (R_{ct}) across the metal/coating interface [25]. This also indicates that the diffusion process has begun even on the first day of measurement. The result is consistent with the Bode plot that shows a slight bend in the mid-frequency range.



Figure 6. (a) Nyquist plot for selected days for PVDF base coating and (b) the focused area in the low frequency region for PVDF base coating. (c)The Bode plot for days 1, 15, and 30 and (d) the equivalent circuit used to fit the data where R_s is solution resistance, R_{po} is pore resistance, R_{ct} is charge transfer resistance, C_c is coating capacitance and C_{dl} is double layer capacitance.

At the third day, under-film corrosion becomes obvious with the presence of a full semi-circle in the Nyquist plot and the appearance of a resistive region in the Bode plot. As time passes, the semi-circle diameter, which consists of the C_{dl} and R_{ct} elements, increases at the end of the 30-day measurement. The corrosion rate decreases as the R_{ct} increases, which is due to the formation of corrosion products or the depletion of the corrosion reaction at the active sites under the coating [26].

The poor barrier properties can be explained by examining the coating structure. Although the base provides a physical barrier between the electrolyte and metal surface, water permeation still occurs due to the presence of micro-pores from the volatilization of the solvent during the heating process [25]. On its own, the base coat offers lower barrier protection against corrosive ions, thus making it an inefficient coating.

3.4.2. EIS Analysis of the Coating System

The electrochemical behavior of superhydrophobic coating is discussed in this section. The scattering of the impedance data in the lower frequency range (Figure 7a) was observed on the first day, despite immersion in the solution 24 h before measurement. Although scattered, the plots roughly formed a part of the semicircle. It is not possible to get a perfect fit from the scattered plot, therefore the values obtained on the first day were only estimates. The scattering of EIS data of the hydrophobic coating was also observed in other studies [18,27] and this is likely due to the presence of air bubbles on the coating/electrolyte interface due to the super-hydrophobic surface. During measurement, the bubbles could collapse and be diffused out of the system, causing agitation and system instability. The scattering of the data occurs throughout the measurement timescale but becomes less scattered at higher frequencies, as shown in Figure 7.



Figure 7. (**a**) Nyquist and (**b**) Bode plot of electrochemical impedance spectroscopy (EIS) measurement for selected days for sample C1 and (**c**) the equivalent circuit.

The super-hydrophobic surface topography consists of peaks and valleys as described in the previous section (Section 3.3). Assuming that the surface within the confined area conforms to the hierarchical structure, a layer of air bubbles will form upon exposure to the electrolyte. These air bubbles obey the Cassie-Baxter state and ideally the layer will hinder the movement of corrosive ions from reaching the coating surface. Unfortunately, this is not the case in the real coating environment, with the presence of different surface characteristics and defects. There are also the performance and stability issues, since water penetrates into the layer after prolonged exposure and the corrosive solution will eventually wet the coating surface.

As the measurement progresses, the plot in Figure 7 was smoother as the air bubbles were released, making the surface fully wetted. The semi-circle diameter decreased due to the decrease in the ohmic resistance, which represents the decrease of barrier properties of the coating [26]. In contrast, an increase in the semi-circle diameter indicates an inhibition process by the corrosion product.

These behaviors are observed in the Nyquist plot in Figure 7, although the semi-circle differences are small. Towards the end of the measurement, the impedance modulus at low frequency is higher than $10^8 \Omega$ cm². These changes are small over long exposure times implying a long-term protection by the coating. The final pore resistance, R_{po} is 3.98×10^9 , with a CPE and the fractional power of frequency, n of 8.23×10^{-10} and 0.81227, respectively.

Figure 8 represents the samples Nyquist and Bode plot for the first and the final day of measurement. The coatings behave similarly as the plot is scattered and becomes smoother by the end of the measurement. The decrease of Nyquist diameter and impedance modulus suggest that the coating experience water penetration. However, the coatings penetration and inhibition process happen on a different time frame, which highly depends on the individual coating properties. A more hydrophobic coating shows larger impedance value but the differences between samples are small considering the small WCA.



Figure 8. EIS data for the first day and day 30; (**a**) Nyquist and (**b**) Bode plot for the samples on the first day of measurement. The data is scattered and roughly forms semicircle. (**c**) Nyquist and (**d**) Bode plot on day 30 of measurement shows data is more defined and smoother.

The synergetic effect between super-hydrophobicity, longer diffusion path, as well as the barrier effect gives a superior performance for the super-hydrophobic coating. The air layer from the super-hydrophobic effect delays the electrolyte penetration. The longer delay offers better protection though it is unknown how long the effect will occur. This requires a more detailed study to determine the stability and length of the effect. This is especially important for applications in an enclosed space or underwater environment. In addition, the top layer that consists of the fn-Al₂O₃ and PVDF covers the base micro-pores, which hinder rapid ion penetration. The fn-Al₂O₃ particles also increase the overall diffusion path, therefore slowing the electrolyte penetration to reach the metal substrate. The latter is known as the barrier effect where the base layer forms a barrier to isolate the substrate from the corrosive environment [28]. Since all polymeric coatings are permeable to corrosive ions, the barrier effect is proportional to the thickness of the coating. With regards to the base behavior discussed in the previous section, the barrier effect is the most insignificant in the overall synergy.

3.4.3. Corrosion Measurements

Potentiodynamic polarization measurement was conducted to assess the corrosion rate and is presented in Figure 9. The value of $I_{\rm corr}$ obtained for the base coat was 1.17×10^{-10} A cm⁻² but

decreases to 1.67×10^{-11} A cm⁻² for coating C1. The lower I_{corr} value corresponds to a greater corrosion resistance of the coating [29].



Figure 9. Tafel plots for all the sample after potentiodynamic polarization measurement on the 30th day.

Table 3 summarizes the corrosion current density and the respective corrosion rate. E_{corr} value is also presented in the table. E_{corr} corresponds to a material property in a given environment which we will not discuss further. The results confirm that the corrosion rates of the specimens coated with the coating system are lower compared to the uncoated carbon steel (0.023 mm/year) [30] and suggests that the coating offers greater protection against corrosion. The value increases when the sample is less superhydrophobic, thus demonstrating the importance of super-hydrophobicity in the inhibition of the corrosion process.

Sample	$I_{\rm corr}$ (A cm ⁻²)	$R_{\rm p}$ (Ω)	$E_{\rm corr}$ (V)	Corrosion Rate (mm/year)
PVDF base coat	11.7×10^{-11}	6.26×10^7	-0.536	13.6×10^{-7}
C1	1.67×10^{-11}	2.13×10^{7}	-0.951	0.62×10^{-7}
C2	2.29×10^{-11}	2.90×10^{7}	-0.762	0.85×10^{-7}
C3	2.82×10^{-11}	2.54×10^{7}	-1.007	1.04×10^{-7}
C4	2.82×10^{-11}	1.42×10^7	-1.381	1.04×10^{-7}
C5	2.78×10^{-11}	5.68×10^7	-0.777	1.21×10^{-7}

Table 3. Corrosion currents and the respective corrosion rates of the prepared coatings.

The quality of the coating system is shown in Figure 10, where the exposed area and the respective optical images were recorded at the end of the 30-day measurement. The images show no sign of degradation or coating breakdown, which coincide with a smaller corrosion rate. In some of the coatings, tiny black dots are observed, which is possibly due to localized pinhole corrosion. This result is consistent with the coating behavior described in the previous section.



Figure 10. Picture of the exposed area on day 30 for sample (**a**) C1, (**b**) C2, (**c**) C3, (**d**) C4, (**e**) C5, and their respective optical micrograph (100×). The red arrow shows a possible pinhole corrosion area.

4. Conclusions

We have successfully fabricated an amphiphobic coating using a functionalized Al₂O₃-PVDF coating system for protection against corrosion. The properties of the coating depend on the amount of the FAS functionalization agent where a higher amount of FAS decreased the quality of the coating. The functionalization was verified using FTIR while the WCA measurement demonstrates a high repellency against water and n-hexadecane. The coating became less repellent with increasing FAS, where the maximum amount of FAS is 0.3 mL (sample C3) before it loses its super-hydrophobicity. FE-SEM images reveal hierarchical structures prominently in C1, and the surface becomes smoother with higher FAS amount. All the coating managed to maintain the protective property for 30 days from the EIS and polarization measurement. EIS analysis of the base layer indicates that the diffusion process began almost instantaneously, and by the third day, under-film corrosion can be observed. Contrastingly, the data for superhydrophobic coating are scattered due to the presence of air bubbles but becomes less throughout the measurement timescale. The small changes in the Nyquist plots and high impedance modulus in the low-frequency area implies long-term protection by the coating. The inhibition behavior is similar for all the coating system; however, the most super-hydrophobic sample offer the highest protection. This finding confirms the advantage of hydrophobicity in corrosion inhibition process. Although a very low corrosion rate was achieved from the coating, it would be of great interest to explore the stability of the super-hydrophobic coatings, especially in confined environments such as in a pipeline or a tanker. Other important aspects of the coating such as adhesion, wear, and ease of processing require further investigations before a super-hydrophobic coating with superior anti-corrosion performance will be ready for real applications.

Supplementary Materials: The following are available online at http://www.mdpi.com/2079-6412/10/4/387/s1, Table S1: Equivalent circuit value for PVDF base coating, Table S2: Equivalent circuit for coating C1, Table S3: Equivalent circuit for coating C2, Table S4: Equivalent circuit for coating C3, Table S5: Equivalent circuit for coating C4, Table S6: Equivalent circuit for coating C5, Video S1: Coating superhydrophobicity in action.

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