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A rapid one-step preparation method of the repairable three-dimensional antifouling superhydrophobic 2.5EPZF coating on magnesium alloys

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Abstract:

Although three-dimensional (3D) superhydrophobic coating has been gradually prepared on the surface of metal substrate for anticorrosion and antifouling, their complex preparation steps and equipment requirements limit their practical application. Herein, by a rapid one-step spray preparation method the fabricating 3D superhydrophobic 2.5EPZF (2.5 g epoxy resin/polycaprolactone (PCL)/zinc oxide/perfluorodecyltriethoxysilane) coating is prepared. This method utilizes a certain

degree of directional arrangement of macromolecular long chain polymers (PCL) as solvent evaporation during the spraying process to form a filamentous structure to construct the 3D coating. This preparation mechanism provides us a novel theoretical guidance method for preparing 3D coating. Further, the silk thickness and mesh density of the 3D mesh structure is controlled by adding epoxy resin. When the amount of epoxy resin is 2.5 g, the surface of 2.5EPZF coating is with about 1-3 μm thick branch frame and 0.1-0.4 μm thin treetop. And the water-contact angle (CA) of 2.5EPZF is 156.6 ± 1.5° and the sliding angle (SA) is < 10° . The 2.5EPZF coating exhibits durable antifouling, strong mechanical&chemical durability, and corrosion resistance. The corrosion current of the 2.5EPZF coating for 0 day's immersion and 35 days' immersion in NaCl solution is 1.043 x 10^{-12} A•cm^{-2} and 1.1703 x 10^{-11} A•cm^{-2}, respectively. Under solar irradiation and at 50 °C for 30 min, the 2.5EPZF coating is with scratching recovering. Additionally, the composite coating can be prepared by a large area. It is expected that this method is readily used and shows great application potentials.

Keywords: PCL, Epoxy, Magnesium alloys, three-dimensional coating, superhydrophobic, anticorrosion and antifouling

1. Introduction

As a solar irradiation structural metal material, magnesium alloys have been widely used in automation industry, ship and automobile, aerospace, missile vehicle, electronic and electrical appliances, etc., due to its outstanding physical and mechanical properties, non-magnetic properties and good thermal dissipation [1-11]. In the field of marine automobile, magnesium alloys are used as instrument panel, steering wheel, gearbox, oil sump, gear box, cylinder cover, seat frame, deck and some wheel hubs, special vessels such as small investigation and experiment ships use magnesium alloys as the hull shell structure and so on [12-18]. However, the poor corrosion resistance of magnesium alloys, especially in the sea environment containing chloride ions, limits the application of magnesium alloys as solar irradiationweight materials for medium and large ships [19-22].

At present, the superhydrophobic coating prepared by one-step method usually was the two-dimensional (2D) coating, such as the epoxy resin (EP)/polymethylhydrosiloxane (PMHS)/modified nano-SiO_2 layer [23], the Maleic anhydride (MAH)/Epoxy resin grafted with fluorine containing side chains (FEP) coating [24], Epoxy resin (EP)/Polydimethylsiloxane (PDMS)/SiO_2 coating [25], and

so on. The stability of the superhydrophobic coating maintains the continuous air film to prevent the invasion of the corrosive media. Compared with 2D coating, the hydrophobic coating with three-dimensional (3D) micropore structure could anchor the air film more tightly in dynamic condition. The current creation of materials with 3D structures often adopts multi-step method (the preparation of fluffy ZnO rods/PDMS by spraying, hydrothermal method and modified by 1H,1H,2H,2H-perfluorooctyltriethoxysilane [26]), sophisticated and special equipment, such as template method, foaming method, adding primary structural particles of specific shape (nanotube, filamentous, needle-shaped, four-corner needle-shaped, etc.), or adopting electrostatic spinning (the preparation of PCL/MSO/SiO_2 hierarchical superhydrophobic mats [27] and Polydimethylsiloxane (PDMS)-modified PCL membranes by electrospinning [28]), 3D printing, optical or laser etching [29-32]. These preparation methods are complicated in steps and long in cycle, or utilize special equipment with high requirements for electrospinning machines, 3D printers, lithography machines and other equipment, which is not convenient for large-area preparation, and is limited by the special structure and shape of the matrix, which is not conducive to large-scale promotion and application [30, 33, 34].

This work explores the use of the simple one-step spray method to generate three-dimensional reticulated porous 2.5EPZF composite coating on magnesium alloy substrate.

PCL, as a semi-crystalline non-toxic biodegradable polymer, is widely used in food packaging, drug release materials, biological implant materials and so on because of its certain hydrophobicity, excellent rheological properties and considerable toughness [22,35]. PCL can form three-dimensional reticulated and porous coating by spraying as a forming component. Epoxy resin (EP) is a thermosetting resin with excellent overall performance. It has good adhesion performance, outstanding corrosion resistance, excellent chemical resistance, low shrinkage characteristics, easy to process and low costs to be widely used in coating, adhesives and other fields [36-38]. Herein, the epoxy resin is as a molding control function, which can control the pore size and porosity of the three-dimensional network structure. Zinc oxide (ZnO) nanoparticles have the characteristics of safety, non-toxicity, high stability, strong photoelectric performance and good antibacterial activity, which are widely used in optoelectronic devices, environmental remediation, food packaging, coating rubber and other industries [39-41]. In this work, ZnO nanoparticles play an essential role in the

construction of micro-nano structure and the attachment of low-surface energy substances, improving the coating roughness and facilitating the uniform distribution of low-surface energy substances. 1H, 1H, 2H, 2H perfluorodecyltrichlorosilane (PFDTES) is a kind of fluorinated organic silane with low surface energy. In this paper, PFDTES is used to reduce the surface energy of materials, to improve the hydrophobicity and corrosion resistance of coating, and restrain the marine bacteria adhesion and fouling [42-45].

In this work, the superhydrophobic 2.5EPZF composite coating was prepared by one-step spraying method. The directional arrangement mechanization of macromolecular long chain polymers (PCL) as solvent evaporation during the spraying process to form a filamentous structure to construct provided a new preparation pathway to prepare the 3D coating. And this method could be used for large-scale 3D coating's preparation without the limitation of the substrate's shape.

2. Experimental Section

2.1. Materials

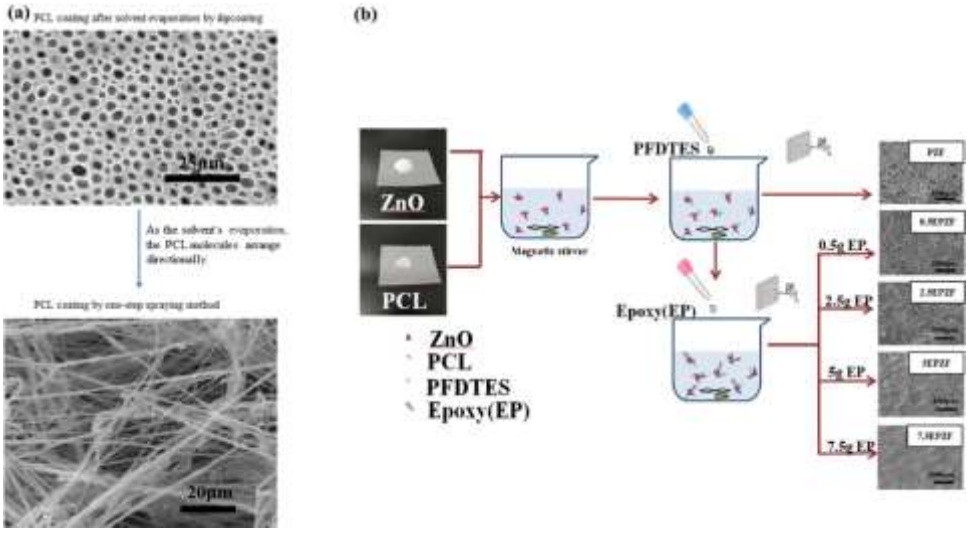
Dichloromethane (DCM) (Qingmei Chemical Reagent Factory, China), 1H,1H,2H,2H-perfluorodecyltriethoxysilane (PFDTES) (Guangzhou Hongcheng

Biotechnology Science and Technology Co., LTD, China, 97%), PCL (Mw: 80,000, Solvay Specialty Polymers, China), ZnO powders (30nm, Beijing Shenghehaoyuan Tech. Co. Ltd., China) and Die-cast AZ91D magnesium alloy (Dongguan Qingmei Metal Materials Co., Ltd., China) were used as the experimental materials. All chemicals were used without further modification.

2.2. Sample preparation

Die-casted Mg alloy (AZ91D) with a chemical composition (wt.) of 8.77% Al, 0.74% Zn, 0.18% Mn, 90.31% were cut into 50 mm x 25 mm x 5 mm. The samples were polished by silicon carbide papers from 150 to 1000 mesh. Then the samples were ultrasonically cleaned in acetone rinsed by de-ionized water, and dried at 60 ºC for the following coating preparation.

2.3. Preparation of composite coating



Scheme 1. The SEM of the PCL coating by dipcoating&spraying method (a) and the preparation process of the composite coating (b).

As shown in Scheme 1a, the PCL coating prepared by dipping would exhibit a regular multi-layernetwork structure in our former researches [46]. And we consided that the mechanism production of the regular network structure was the macromolecular long chain polymers (PCL) occurred a certain degree of directional arrangement during solvent evaporation. After multiple experiments, a three-dimensional network structure coating of PCL was prepared by simple spraying method as shown in Scheme 1a. By the same method, added ZnO nanoparticles (5 g, 6.14 x 10^{-2} mol), PFDTES (1 mL, 2.00 x 10^{-3} mol) to the PCL solution (PCL 5g, 6.25 x 10^{-5} mol, Dichloromethane (DCM, as the solvent), 80 mL) during the mixing process under vigorous stirring with a magnetic stirrer at RT as shown in Scheme 1b. Then, epoxy (EP) (0.5 g, 2.5 g, 5 g, 7.5 g) was added to the solution, respectively. The stirring process lasted for 1 hour. Then the polycaprolactone/epoxy resin/zinc oxide/perfluorodecyltriethoxysilane (EPZF) composite coating was prepared on the treated magnesium alloy substrate by one-step spray method under appropriate pressure with the stirred solution. After that, all samples were in the air at RT. for 24 h to dry and solidify. The PZF (polycaprolactone/zinc

oxide/perfluorodecyltriethoxysilane) coating was prepared by the same process as the control groups. The preparation conditions and the stirred solutions of samples with composite coating were shown in the table 1.

Sample	Stirred solutions	Preparation conditions
PZF	80 g DCM, 5 g PCL, 5 g ZnO, 1mL PFDTES	Room temperature 45 s
0.5EPZF	80 g DCM, 5 g PCL, 5 g ZnO, 1mL PFDTES, 0.5 g EP	
2.5EPZF	80 g DCM, 5 g PCL, 5 g ZnO, 1mL PFDTES, 2.5 g EP	
5EPZF	80 g DCM, 5 g PCL, 5 g ZnO, 1mL PFDTES, 5 g EP	
7.5EPZF	80 g DCM, 5 g PCL, 5 g ZnO, 1mL PFDTES, 7.5 g EP	

Table 1. The preparation conditions and the stirred solution of samples with composite coating.

2.4. Analysis of composite coating

The surface morphology of the prepared coating was observed by using scanning electron microscopy (SEM, VEGA3, Tescan Co. China Ltd., China) equipped with energy-dispersive spectrometer (EDS). The water contact angle (CA) was measured at room temperature using an optical contact angle meter (Dataphysics OCA 15EC, Germany) with a 5 μL water drop. Electrochemical tests were performed by electrochemical workstation (CorrTest CS350). The surface roughness of samples was measured by laser confocal microscope (CLSM) (VK-X1000, Keyence, Japan). The bacterial adhesion test was measured by using Bacillus subtilis CMCC (B) 63501 (Shanghai Luwei Technology Co., Ltd., China) at 120 rpm at 30 ºC for 20 days. Subsequently, the samples were observed by SEM and digital camera to measure the Bacillus adhesion status and the surface corrosion resistance features. Then, the FTIR analysis of the coating was measured by Thermoscientific (Summit Pro, USA). Further, the samples' mechanical adhesion, self-cleaning ability, abrasion resistance and pH

durability, Bacillus subtilis adhesion and Solar irradiation&thermal repair were measured in our study. Three parallel samples were measured in the test progress.

3. RESULTS AND DISCUSSION

3.1. Surface characteristics

The SEM surface morphology of PZF, 0.5EPZF, 2.5EPZF, 5EPZF, 7.5EPZF samples was shown in Figure 1. The coating of PZF (Figure 1a and b) and 0.5EPZF (Figure 1c and d) exhibited a three-dimensional surface with network structure and high porosity. With the addition of 0.5 g epoxy resin, the samples were with lower porosity and the ZnO particles were dispersed in network structure. Then with the increase of epoxy resin content, the 2.5EPZF (Figure 1e and f) sample was with spatial wire mesh-like skeleton structure and lower porosity. The diameter of mesh and skeleton of 2.5EPZF sample were about 0.1-0.4 μm and 1-3 μm. After that, with more addition of epoxy resin content, the network and porous structure of the 5EPZF (Figure 1g and h) and 7.5EPZF (Figure 1i and j) samples disappeared and the surface of 7.5EPZF samples became smooth.

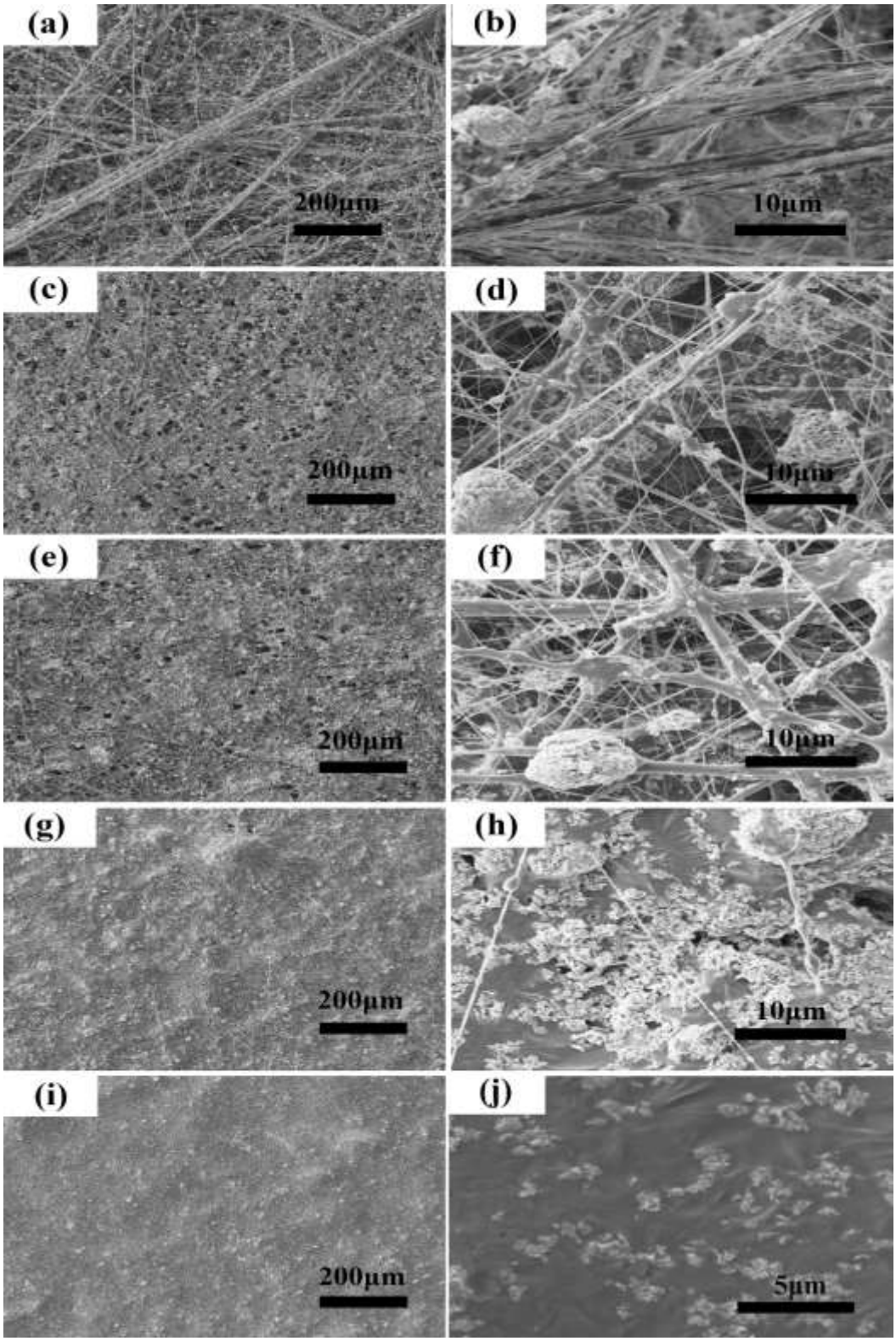


Figure. 1. The SEM images of PZF (a and b), 0.5EPZF (c and d), 2.5EPZF (e and f), 5EPZF (g and h), 7.5EPZF (i and j) samples.

The cross section SEM image of PZF (Figure 2a) and 0.5PZF (Figure 2b), 2.5EPZF (Figure 2c), 5EPZF (Figure 2d), 7.5EPZF (Figure 2e) samples were shown in Figure 2.

172 The thickness of PZF (Figure 2a) and 0.5PZF (Figure 2b), 2.5EPZF (Figure 2c),
173 5EPZF (Figure 2d), 7.5EPZF (Figure 2e) were about 137 μm, 178 μm, 77 μm, 84 μm
174 and 108 μm, respectively. PZF and 0.5PZF samples were with three-dimensional
175 network and porous structure. With the addition of 0.5 g EP, the coating thickness of
176 0.5EPZF (Figure 2b) sample was with significant increase. It was because the support
177 force of the filamentous structure between layers increased under 0.5 g addition of EP.
178 With the continue adding of EP content, the coating thickness of 2.5EPZF sample
179 became thinner markedly to 77 μm (Figure 2c). And the reason was that the thin silk
180 became thicker and the combination of filamentous structures between layers becomes
181 tighter with 2.5 g EP addition. And then with the addition of 5 g EP and 7.5 g EP the
182 thickness of composite coating gradually increased to 84 μm (Figure 2d) and 108 μm
183 (Figure 2e). With the addition of 5g and 7.5 g EP, the network and porous structure of
184 the 5EPZF and 7.5EPZF samples almost disappeared. When the addition of 5 g and 7.5
185 g EP could fully fill the pore, the thickness of the coating increased as the increasing
186 amount of EP.

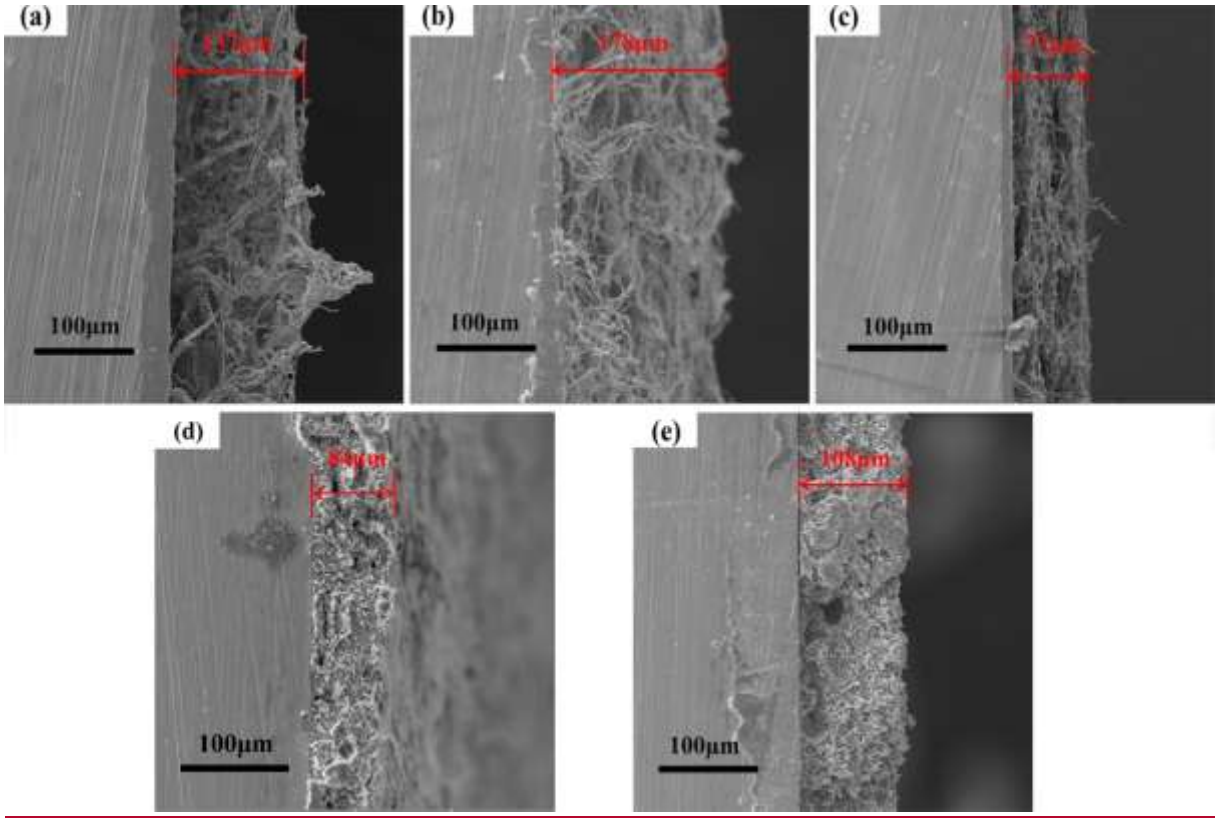


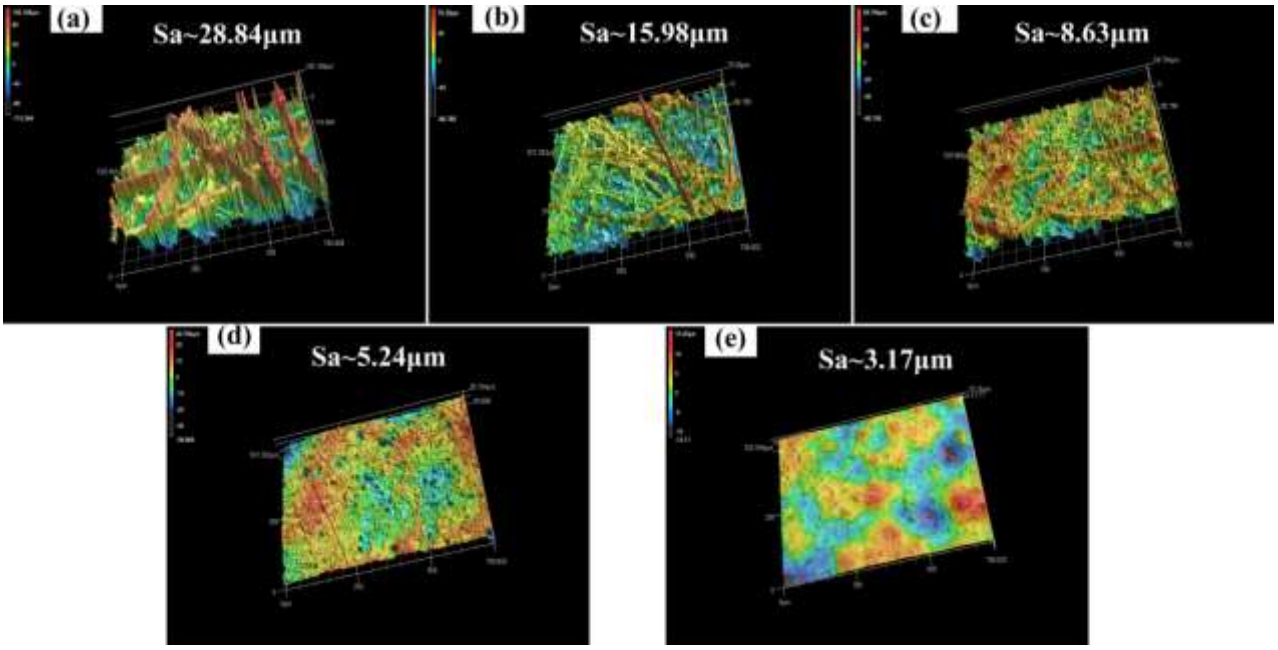
Figure. 2. The cross section SEM images of PZF (a) and 0.5EPZF (b), 2.5EPZF (c), 5EPZF (d), 7.5EPZF (e) samples.

3.2. Surface roughness characteristics

Moreover, roughness measurement with laser confocal microscope (VK-X1000, Keyence) and the 3D morphology of the samples of PZF (Figure 3a), 0.5PZF (Figure 3b), 2.5EPZF (Figure 3c), 5EPZF (Figure 3d), 7.5EPZF (Figure 3e) samples was shown in Figure 3. The surface roughness of PZF (Figure 3a) and 0.5PZF (Figure 3b), 2.5EPZF (Figure 3c), 5EPZF (Figure 3d), 7.5EPZF (Figure 3e) samples were 28.84 μm，15.98 μm, 8.63 μm, 5.24 μm and 3.17 μm. The change of coating roughness showed that the roughness of composite coating decreased obviously with the increase of epoxy resin content. When the amount of epoxy resin was 7.5 g, the 7.5EPZF

199 composite coating was almost flat which was consistent with the results observed in

200 Figure 1i and j.



201

202 **Figure. 3.** The 3D morphology of the PZF (a) and 0.5PZF (b), 2.5EPZF (c), 5EPZF (d), 7.5EPZF (e) samples.

203 *3.3. Wetting behaviors*

204 The wettability of liquid droplets is an essential indicator to measure the protective

205 properties of the coating. The hydrophobic performance can significantly prevent

206 corrosive media and wetting, and prolong the service life of the coating. The contact

207 angle (CA) of the coated samples was tested by the contact angle tester (Dataphysics

208 OCA 15EC, Germany). The volume of the drops of deionized water was 5μl. The

209 5-point measurements were tested for each sample. The contact angle test results of

210 PZF, 0.5PZF, 2.5EPZF, 5EPZF, 7.5EPZF were shown in Figure 4.

In Figure 4a the contact angle test showed that the CA of the PZF composite coating was 143±1.3°. The PZF composite coating did not reach the superhydrophobicity (150°). As shown in Figure 1a and b, the reason was that the PZF coating was a loose porous structure and the excessive distance between the PZF silk made the hydrophobic air film discontinuous. With the increase of epoxy resin content, the contact angle began to increase. The CA of 0.5EPZF and 2.5EPZF composite coating were 152.2 ± 1.6° (Figure 4b) and 156.6 ± 1.5° (Figure 4c), respectively. And the SA of 2.5EPZF composite coating was < 10°. As the amount of epoxy resin continued to increase, the CA of the composite coating decreased. The CA of the 5EPZF composite coating and 7.5EPZF composite coating decreased to 151.3 ± 1.6° (Figure 4d) and 129.7 ± 2.1° (Figure 4e), respectively. It illustrated that the composite coating changed from superhydrophobic to hydrophobic.

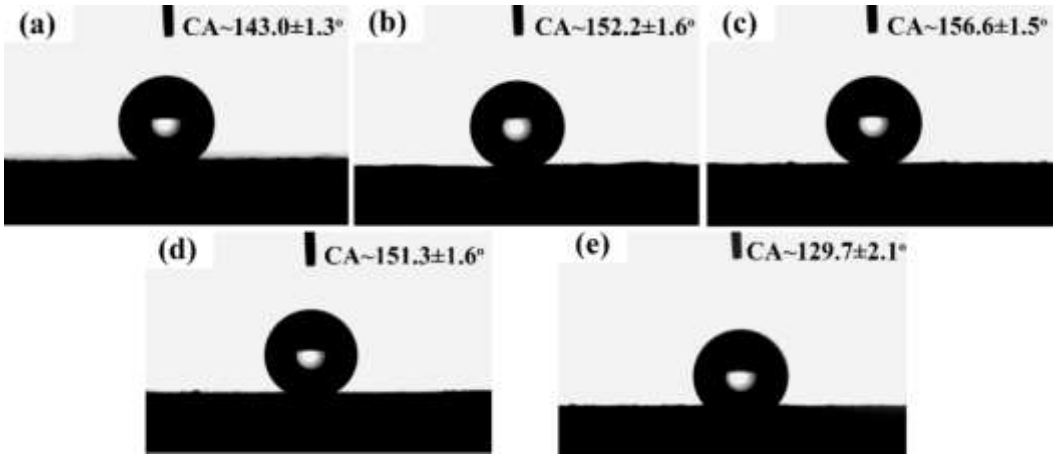


Figure. 4. The contact angle test results of PZF (a), 0.5EPZF (b), 2.5EPZF (c), 5EPZF (d) and 7.5EPZF (e) samples.

226 *3.4. Formation mechanism for the composite coating*

227 The formation mechanism for the composite PZF and EPZF was shown in Figure 5.
228 Without EP, the mixture of PCL, ZnO and PFDTES could form into the filamentous
229 interweaving after the mixture spraying from the spray gun nozzle. It was because the
230 PCL was a long chain macromolecules polymer with fewer branched chains. As the
231 solvent evaporates, the PCL of the mixture would exhibit a certain directional
232 arrangement to form a filamentous structure (Figure 5a). The curing mechanism of
233 epoxy resin was shown in Figure 5d. After curing, epoxy resin was a long-chain high
234 polymer with a three-dimensional configuration and the network structure of EP partly
235 restricted the directional arrangement of long chain molecules (PCL) [39,40].

236 Additionally, the crosslinking of EP improves significantly as the amount of EP
237 reagent added increases. As the addition amount of EP gradually increased, the coarse
238 branch structure duly became thicker and more numerous (Figure 5b). When the
239 addition amount of EP was 2.5 g, the composite coating was with a certain number of
240 0.1-0.4 μm filamentous structure and a significant amount 1-3 μm coarse branch
241 structure (Figure 1e and f, Figure 2c). Furtherore, with the addition amount of EP
242 increased to 5 g and more, the crosslinking degree of epoxy resin continued to increase

and the filamentous structure&coarse branch structure vanished to form an overall block structure coating (Figure 5c). Figure 5e was the hydrolysis of PFDTES [46]. The hydrolysis product of PFDTES would combine with hydroxyl groups (ZnO and EP) to form a modified surface (Figure 5f) [47, 48]. On the other side, due to the hydrophilic group (-OH) of epoxy resin itself, when the amount of epoxy resin reached a certain level, the composite coating became hydrophilic from hydrophobic.

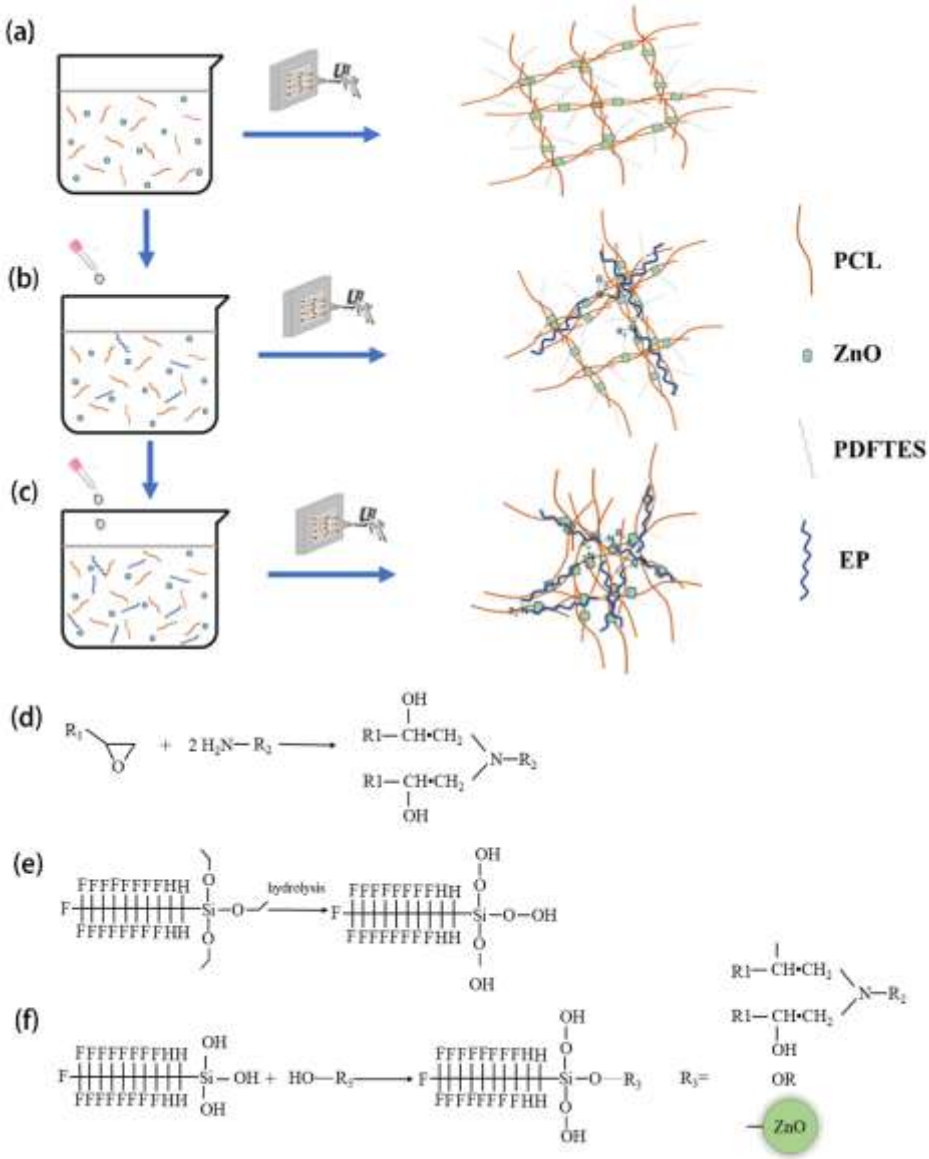


Figure. 5. Formation mechanism for the composite coating of PZF and EPZF composite coating.

3.5. Electrochemical corrosion behavior

With a three-electrode system in 300 mL 3.5 wt.% NaCl electrochemical impedance spectra (EIS) were carried out [49]. Samples were exposed with a surface area of 1 cm^2. A saturated calomel and a platinum mesh electrode were used as the reference and the counter electrode, respectively. At the open circuit potential (Ecorr), the scanning frequency range of electrochemical impedance test was 10^5-10^{-2} Hz, and the amplitude of sine wave disturbance was 10mV. The scanning rate of potentiodynamic polarization curve was 0.5 mV•s^{-1}.

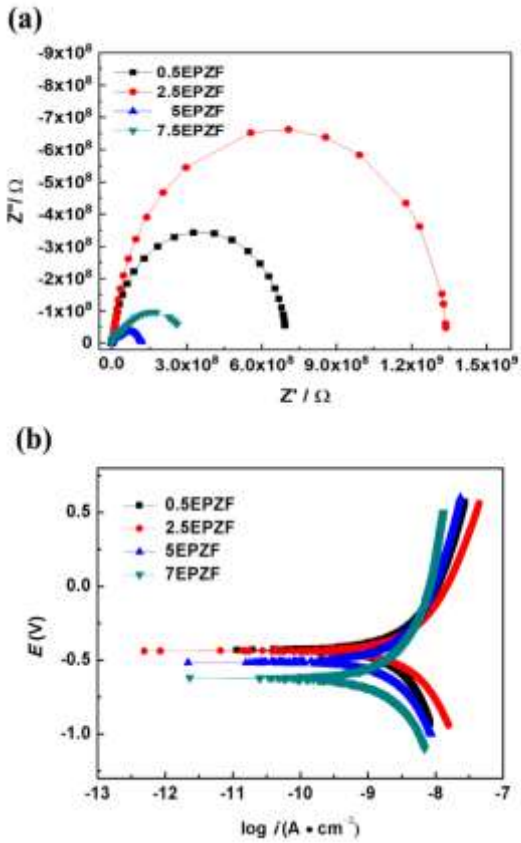


Figure. 6. EIS and potentiodynamic polarization results of EPZF composite coating with different amounts of epoxy resin.

262 Figure 6 showed the EIS (a) and potentiodynamic polarization test results (b) of the
263 composite 0.5PZF, 2.5EPZF, 5EPZF, 7.5EPZF coating respectively. The size of
264 impedance arc could objectively reflect the corrosion performance of the coating. The
265 Nyquist diagram of EPZF composite coating with different amounts of epoxy resin was
266 shown in Figure 6a. With the addition of epoxy resin, the impedance arc was the
267 largest when the amount of epoxy resin is 2.5 g, about 1.37 x 10^9.

Samples	I_{cor} (A/cm^{-2})	E_o (V)	Corrosion Rate (mm/a)
0.5EPZF	6.2351 x 10^{-10}	-0.43216	7.6118 x 10^{-6}
2.5EPZF	1.043 x 10^{-12}	-0.43877	1.2733 x 10^{-8}
5EPZF	1.2716 x 10^{-8}	-0.7174	1.5524 x 10^{-4}
7.5EPZF	5.6863 x 10^{-9}	-0.6224	6.9419 x 10^{-5}

268 **Table 2.** E_{corr}, i_{corr} and Corrosion Rate of the EPZF composite coating on Mg substrate with different amounts
269 of epoxy resin immersed in NaCl aqueous solutions (3.5 wt.%).

270 The electrochemical polarization test showed that with the increase of the amount
271 of epoxy resin, the corrosion current of the coating first decreased from 6.2351 x 10^{-10}
272 A•cm^{-2} (0.5EPZF) to 1.043 x 10^{-12} A•cm^{-2} (2.5EPZF) with the addition of epoxy resin
273 from 0.5 g to 2.5 g. Then with the increase of epoxy resin content to 5.0 g, the
274 corrosion current enhanced while the corrosion performance diluted. It was because
275 with the raise of the amount of epoxy resin to 2.5 g, the network structure of the
276 coating became dense visibly, the porosity decreased significantly, and the proportion
277 of coarse branches increased. The dense pores tightly grasped the air to form a stable

air protection film, and this coating could reach the superhydrophobic state of 156.6 ± 1.5°, making the coating have good corrosion resistance. The thickness of 2.5EPZF composite coating was only 77 μm. However, the 2.5EPZF composite coating had relatively best corrosion protection performance. When the amount of epoxy resin continued to increase to 5 g, the quality of porous structure was with a sharp decline. The contact angle test also showed that the hydrophobic property of the 5EPZF coating decreased demonstrably. The coating thickness of 5EPZF was 95 μm which was thicker than 2.5EPZF, yet the corrosion rate of 5EPZF reduced by over 500 times. When epoxy resin addition was 7.5 g, the porous structure of the 7.5EPZF coating almost disappeared. At the same time, the 7.5EPZF coating was hydrophobic from superhydrophobic. The coating thickness of 7.5EPZF reached 135 μm. It was about 1.6 times the thickness of 2.5EPZF coating, but its corrosion resistance was worse than that of 2.5EPZF coating. It showed that the superhydrophobic three-dimensional porous structure of the thinner composite coating could greatly enhance the corrosion performance.

Here the 2.5EPZF sample was selected as the experiment sample, and magnesium alloy and PZF coating sample was used as the controlled sample for the following

electrochemical performance and adhesion test of marine bacterium (Bacillus subtilis). Figure 7 showed the results of Nyquist impedance and potentiodynamic polarization tests of uncoated magnesium alloy samples, the PZF coating sample and the 2.5EPZF coating sample. EIS and potentiodynamic polarization results illustrated that the 2.5EPZF composite coating had the best corrosion resistance. And the corrosion current of 2.5EPZF sample was 1.043 x 10^{-12} A•cm^{-2}.

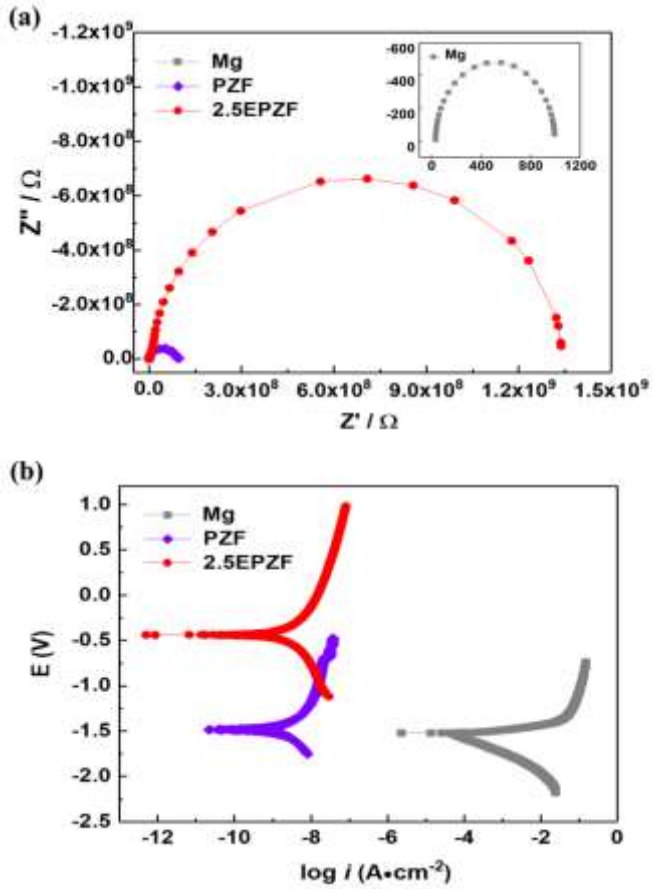


Figure. 7. The Nyquist diagramand and potentiodynamic polarization results of magnesium alloy substrate, PZF and 2.5EPZFsamples.

Samples	I_{cor} (A/cm^{-2})	E_o (V)	Corrosion Rate (mm/a)
Mg	6.4746 x 10^{-5}	-1.5532	1.3951
PZF	2.0373 x 10^{-11}	-1.0388	0.5239 x 10^{-7}

2.5EPZF	1.043 x 10^{-12}	-0.43877	1.2733 x 10^{-8}

Table 3. E_{corr}, i_{corr} and Corrosion Rate of the uncoated Mg substrate, PZF and 2.5EPZF composite coating immersed in NaCl Aqueous Solutions (3.5 wt.%).

Further, the EIS of the 2.5EPZF sample was tested in NaCl Aqueous Solutions (3.5 wt.%) after different immersion times for 0 day, 15 days, 25 days, 35 days at roomtemprature.

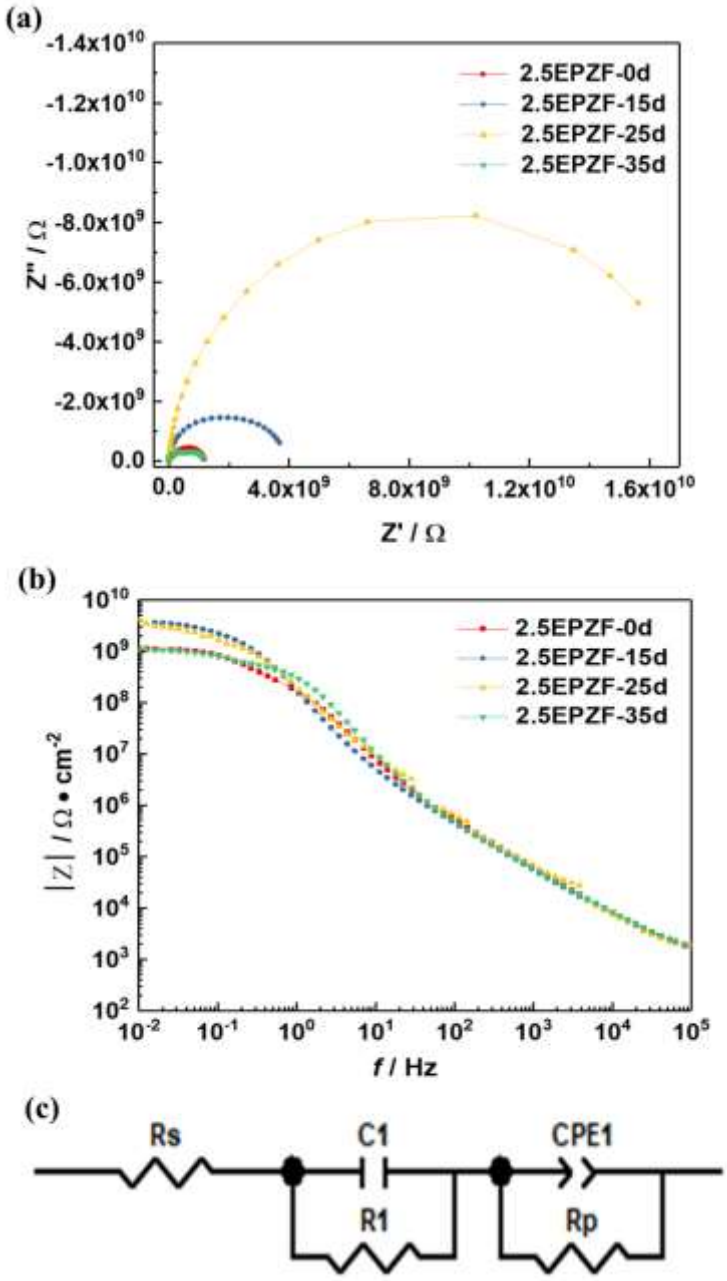


Figure. 8. Bode&Nyquist plots of 2.5EPZF composite coating at different immersion times in NaCl Aqueous Solutions (3.5 wt.%) and the corresponding equivalent electric circuit.

EIS of the 2.5EPZF sample in 3.5% NaCl solution for 35 days immersion was displayed in Figure 8. At the beginning, the Nyquist spectra present an arc with a large radius and the value of the low frequency impedance (|Z|0.01 Hz) in Bode spectra is about 1.37 x 10^9 Ω•cm^{-2}, manifesting high barrier property of the coating to the substrate [50]. As shown in the Nyquist diagram (Figure 8a), for the 2.5EPZF coating, the impedance modulus cut from 1.37 x 10^9 to 3.90 x 10^9 Ω•cm^{-2} severely after 15 days' immersion in NaCl Aqueous Solutions (3.5 wt.%). After 25 days' soaking, the impedance was increased to 1.60 x 10^{10} Ω•cm^{-2}. Under the pressure of the outside force (NaCl Aqueous Solutions), the deformation of treetop occurs and the pores of 2.5EPZF sample with mesh and skeleton coating become denser to grasp the air film firmly. It was caused by the diameter of mesh and skeleton of 2.5EPZF sample with about 0.1-0.4 μm Treetop structure and 1-3μm Branch structure. And the 1-3μm Branch structure of the 2.5EPZF coating provided the sufficient support to maintain the integrity of the air film. After 35 days' immersing, the impedance of 2.5EPZF sample was reduced to 1.30 x 10^8 Ω•cm^{-2}. During this time, the NaCl corrosion media gradually seeped into the surface of the air film with the measurably decrease of the

328 impedance modulus. Furthermore, the air film of 2.5EPZF coating was always present

329 during 35 days' immersion. After 35 days' immersion, the corrosion current of the

330 2.5EPZF coating was 1.1703 x 10^{-11} A•cm^{-2}.

331 Figure 8a, 8b displayed Nyquist and Bode plots of 2.5EPZF specimens after

332 different time's immersion in the NaCl solution (3.5 wt.%). The lowest impedance was

333 related to the 2.5EPZF-35d sample. Nyquist plots for all 2.5EPZF samples with

334 different time immersion consisted of two semi-circles. One semi-circle of the

335 composite coating was related to coating properties in the high-frequency range and

336 another one was attributed to double layers characteristics in the low-frequency range.

337 The Z view software was utilized for corresponding equivalent electrical circuits

338 (Figure 8c). The circuits had various elements such as solution resistance (Rs),

339 charge-transfer resistance (Rp), double layer constant phase element (CPEdl), pore

340 resistance (Rc), and coating constant phase element (CPEc). The highest value of

341 composite coating resistance was related to 2.5EPZF-25d sample (1003 Ωcm^2). The

342 lowest value of CPEp has also corresponded to 2.5EPZF-25d sample (3.008 x 10^{-10}).

343 After 35 days' immersion the impedance of 2.5EPZF-35d sample decreased to below

344 the impedance of 2.5EPZF-0d. It could be owed to the marvelous barrier property of

the superhydrophobic three-dimensional porous structure and after 35 days' immersion the corrosive media was partially wetted the 2.5EPZF coating.

3.6. Protection mechanism for 2.5EPZF composite coating

Figure 9 was the schematic representation of the Load-bearing corrosion protection mechanism for 2.5EPZF composite coating. The three-dimensional structure of 2.5EPZF composite coating was like the Branch and Treetop. As shown in Figure 1f, the 0.1-0.4 μm mesh and 1-3 μm skeleton of 2.5EPZF sample played the role as the Branch and Treetop of the tree, respectively. Under the pressure of the outside force (pressure of the corrosive medium), the deformation of treetop occurs and the pores of mesh and skeleton coating become denser to grasp the air film firmly. Furthermore, the 1-3 μm Branch structure of the 2.5EPZF coating provided the sufficient support to maintain the integrity of the air film. Then the Load-bearing type 2.5EPZF composite coating could afford more durable protection from corrosive media in the case of thinner coating.

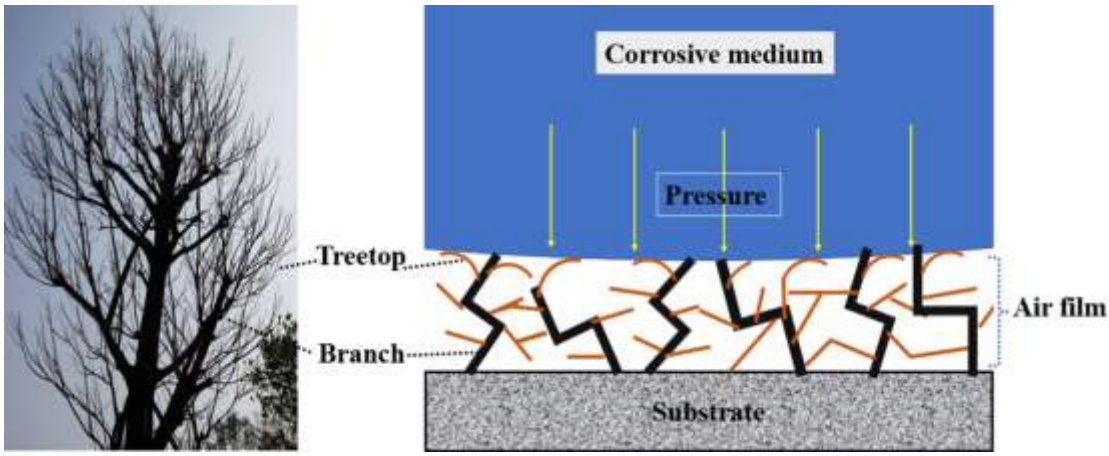


Figure. 9. Schematic representation of the Load-bearing type corrosion protection mechanism for 2.5EPZF composite coating.

3.7. FT-IR spectra of PCL, PZ, PZF and 2.5EPZF coating&mechanical adhesion and self-cleaning tests

The FT-IR spectra of PCL, PZ, PZF and 2.5EPZF coating&mechanical adhesion and self-cleaning tests were shown in Figure 10. The specific functional groups for PCL, PZ, PZF and 2.5EPZF coating were evaluated by FTIR absorbance as shown in Figure 10a. The bands observed at 2960-2870 cm^{-1} and 1725 cm^{-1} were related to tensile vibrations of C-H and Stretching vibrations of the ester carbonyl group, respectively [51, 52]. Furthermore, bands at 1462 cm^{-1} and 1066 cm^{-1} were related to C-C and C-H tension [46]. It was determined that the perceptible signal at 400-600 cm^{-1} increased with the addition of ZnO. The reason was that the ZnO material had an intense IR band centered at 442 cm^{-1} in the spectral region 0-600 cm^{-1} [53]. The absorption bands appearing at 1300 cm^{-1} - 1000 cm^{-1} was attributed to the stretching mode of CF_2 [54].

With the addition of PDFTES, the peaks between 1300 cm^{-1} - 1000 cm^{-1} increased. During solidification of the coating, EP and its cross-linker formed a net, and the PDFTES would move towards the surface during the coat's solidification because the PFDTES was highly hydrophobic and the EP system was hydrophilic [46]. The characteristic absorption peaks of Si-O and O-Si-O appeared at 1035 cm^{-1} and 827 cm^{-1}, which illustrated that the amount of PFDTES on the surface of 2.5EPZF sample significantly increased [55]. It indicated that PFDTES had transferred to the surface of the composite coating with solidification of EP.

Generally, the stability of adhesive materials on the surface is one of the main challenges of coating [56,57]. The adhesion strength between coating and magnesium alloy was evaluated according to ASTM D3359-09 method [49]. The result of adhesion measurement illustrated that the 2.5EPZF coating in Figure 10b showed very few flakes detached at intersections. It suggested that the bonding strength between the 2.5EPZF coating and magnesium sample was strong enough to be potentially used in physiological environments.

Lotus-inspired superhydrophobic surface features self-cleaning effect [58]. The self-cleaning ability of 2.5EPZF coating was evaluated and displayed in Figure 10c.

Due to the SA being less than 10°, water droplets could slide on the surface of the 2.5EPZF sample easily. And the self-cleaning test was measured to evaluate the self-cleaning ability of the 2.5EPZF coating as shown in Figure 10c. The self-cleaning test result illustrated that the sand on the surface of the 2.5EPZF sample was carried away mostly after 10 water droplets, which proved that the composite coating was with good self-cleaning performance.

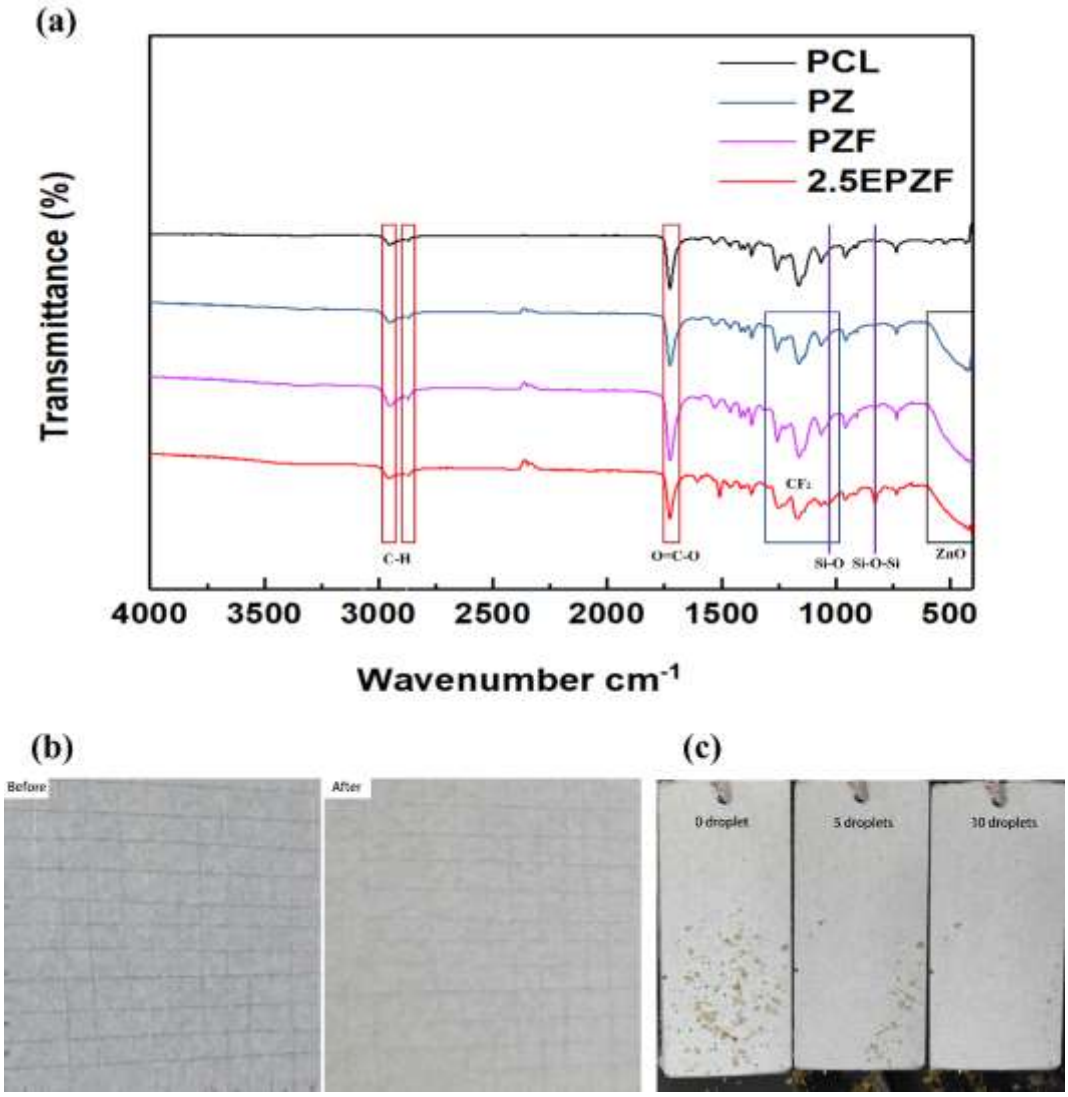


Figure. 10. FTIR analysis of PCL, PZ, PZF and 2.5EPZF coating (a), the results of mechanical adhesion (b) and self-cleaning test (c).

400 *3.8. Abrasion resistance and pH stability test*

401 Figure 11 showed the results of abrasion resistance test and pH durability of
402 2.5EPZF coating. The mechanical abrasion resistance of 2.5EPZF was measured by the
403 sandpaper abrasion test to evaluate the tribological properties [59, 60]. The result of
404 the 2.5EPZF coating's sandpaper abrasion experiment was as shown in Figure 11a. The
405 2.5EPZF coating was abraded on a 1000-mesh sandpaper under a weight of 360.0 g at a
406 constant speed of 1 cm/s. After 3 cycles of total length of 30 cm, the CA of 2.5EPZF
407 coating was 151.1 ± 1.2° with a small amount of debris falling.

408 The contact angle test of the water droplets with different pH values was carried out
409 on the surface of the 2.5EPZF coating to determine the resistance of the coating to acid
410 and alkali solutions. As shown in Figure 9b, the CA of the 2.5EPZF coating surface
411 increased first and then decreased with the increase of pH value, but it is higher than
412 153°. The results indicated that the 2.5EPZF coating had excellent chemical stability.

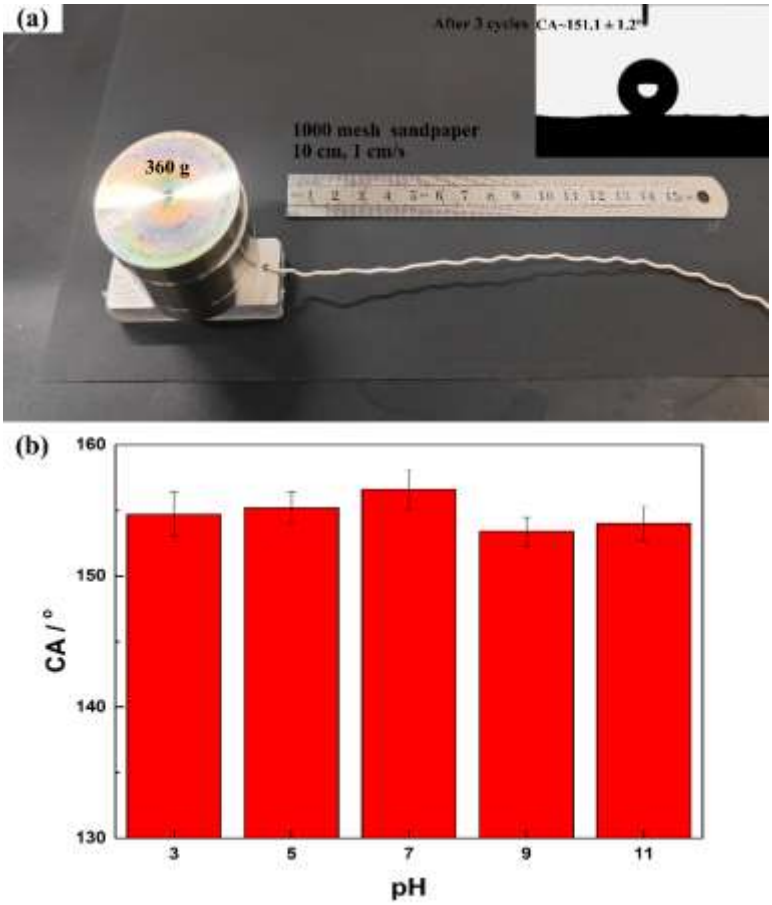


Figure. 11. The mechanical abrasion resistance (a) and pH durability (b) of 2.5EPZF coating.

3.9. Bacillus subtilis adhesion test and corrosion resistance test

Figure 12 showed the results of Bacillus subtilis adhesion test for 20 days at 30 °C and 120 prm and corrosion resistance test in 3.5% wt NaCl at room temperature. In experiment, three parallel samples from each group. After the bacterial adhesion test, the tested samples were fixed in 2.5% glutaraldehyde aqueous solutions for 20 minutes. Then divided them into ethanol solution at 5%, 15%, 25%, 45%, 65%, 85%, 95% of the step concentration in proper order. In the end, dehydrated in anhydrous ethanol for 20 minutes and dried for natural air. Figure 12a, b and c showed the digital photos and

423 SEM images of magnesium alloy substrate, PZF and 2.5EPZF samples after 20 days in
424 Bacillus culture. Figure 12a, 12b and 12c were the digital photos and SEM images of
425 magnesium alloy substrate, PZF and 2.5EPZF samples after the Bacillus subtilis
426 adhesion test. There was the serious corrosion of the AZ91D magnesium
427 alloy substrate as the Digital photo shown. Furthermore, there were many bacilli on the
428 corrosion surface of magnesium alloy as shown in SEM image of Figure 12a. It showed
429 that AZ91D magnesium alloy was prone to corrosion and microbial attachment in the
430 marine environment containing Cl^- and marine bacteria (Bacillus). There were the
431 perceptible coating damage and measurably bacillus adhesion of the magnesium
432 substrate in the Bacillus environment for 20 days' immersion in Figure 10a. Compared
433 with the magnesium alloy substrate, the PZF coating was damaged partially and the
434 pitting pits were produced. It showed that the degradable PCL combined with PFDTES
435 could not provide sufficient protection for magnesium alloy in the marine environment
436 containing Cl^- and marine bacteria (Bacillus). In Figure 12b, the SEM image of some
437 residual PZF coating illustrated that the PZF coating had a good anti-adhesion effect
438 against Bacillus. Figure 12c was the digital photo and SEM image of the 2.5EPZF
439 composite coating sample after 20 days' immersion in the Bacillus environment. The

results showed that the 2.5EPZF composite coating had no obvious surface damage and corrosion. The protective 2.5EPZF coating was still intact and the three-dimensional structure of the coating was also maintained. What's more, there was no obvious bacillus adhesion. It showed that 2.5EPZF composite coating could provide sufficient protection for magnesium alloy samples and had strong adhesion resistance to marine bacteria Bacillus.

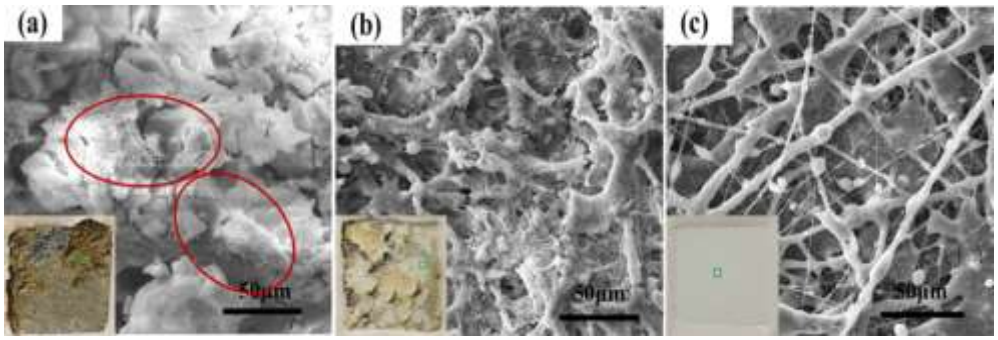


Figure. 12. Digital photos&SEM images of magnesium alloy substrate (a), PZF (b) and 2.5EPZF (c) samples after 20 days in Bacillus culture at 30°C: magnesium alloy substrate.

3.10. Solar irradiation and thermal repair, grid corrosion test

Drew a big cross on the surface of superhydrophobic 2.5EPZF composite coating with a surgical blade. The scratch depth exposed the magnesium alloy, and the scratch width was about 20-25 μm. A group of crossed 2.5EPZF composite coating samples were exposed to outdoor direct sunsolar irradiation for 6 hours (Wuhan, September). Another group of crossed 2.5EPZF composite coating was placed in an oven at 50 °C for 30 min, and then took out to the air and cooled to room temperature. The crossed

2.5EPZF samples without solar irradiation or heating were used as the control group. During the accelerated corrosion test of scratched 2.5EPZF samples, the above three groups of samples were placed in the 10% wt NaCl solutions at 30 °C for 24 hours. After that, took them out to the outdoor environment for 20 days to observe the surface changes of the samples (as shown in Figure 13). The 2.5EPZF samples before (Figure 13a) and after (Figure 13d) grid corrosion test and the SEM image (Figure 13g) illustrated that the 2.5 EPZF composite coating could provide protection for magnesium alloy matrix, and only corrosive medium infiltration occurs at the scratch. The 2.5EPZF samples under 6 hours' solar irradiation before (Figure 13b), after (Figure 13e) grid corrosion test and the 2.5EPZF samples at 50 °C for 30min before (Figure 13c), after (Figure 13f) grid corrosion test showed that there was no corrosive medium infiltration at the scratch. It showed that 2.5EPZF sample would be repaired to a certain extent after sunsolar irradiation or at 50 °C for 30 min to prevent the corrosion damage of corrosion medium NaCl to the sample.

The EDS data (Table 4) showed that the content of Si and F of 2.5EPZF coating increased significantly after illumination and heating at 50 °C. Under the solar irradiation or heating at 50 °C, the PFDTES on the coating surface would undergo a

certain amount of molecular transfer and the redistribution of perfluorinated branched chains, which would repair the scratch gap to a certain extent, increase the hydrophobicity, reduce the invasion of corrosive media, and improve the corrosion protection ability of scratches.

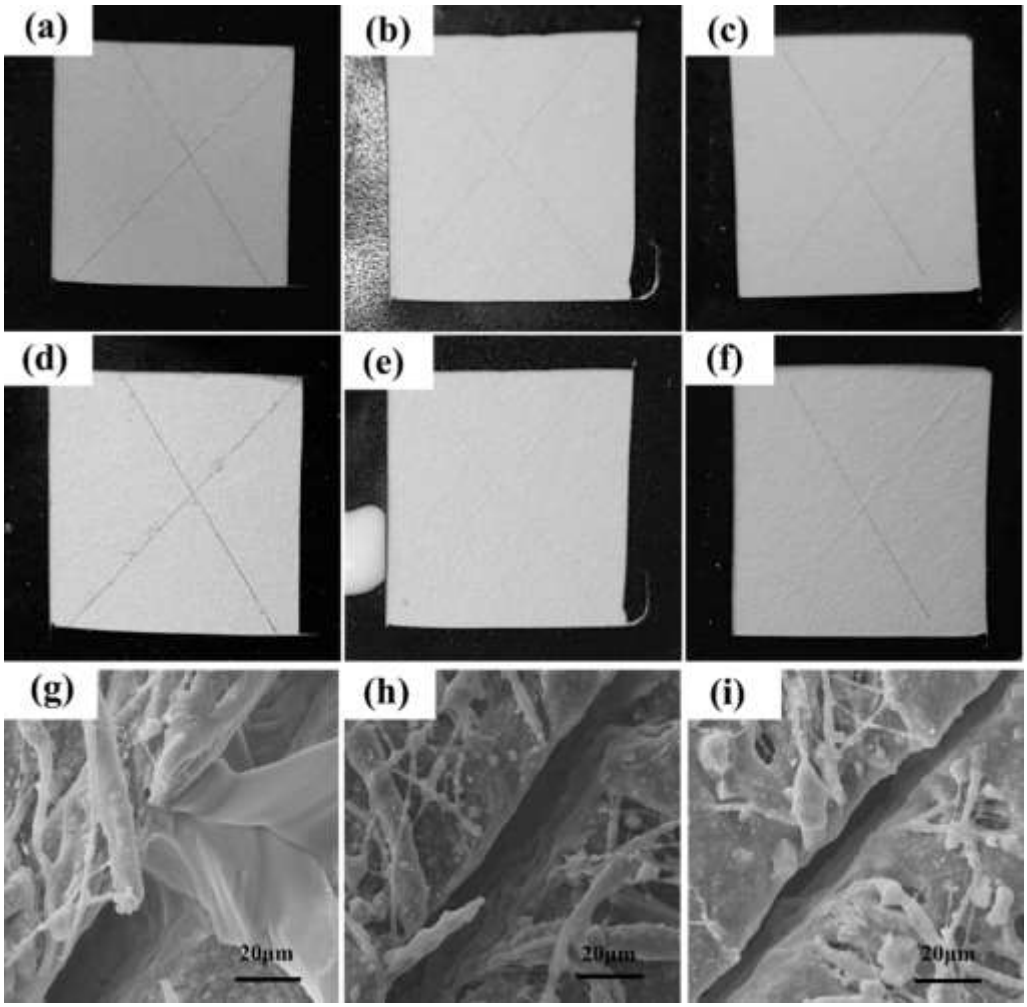


Figure. 13. Digital photos scratched 2.5EPZF samples before&after grid corrosion test, 2.5EPZF samples at 50 °C for 30 min before (c)&after (f) grid corrosion test and the SEM of sample of scratched 2.5EPZF after accelerated corrosion test; 2.5EPZF samples before (a)&after (d) grid corrosion test; 2.5EPZF samples under solar irradiation before (b) and after (e) grid corrosion test; 2.5EPZF samples at 50 °C for 30 min before (c) and after (f) grid corrosion test and the SEM of sample of scratched 2.5EPZF after accelerated corrosion test; 2.5EPZF samples under solar irradiation before (b) and after (e) grid corrosion test; 2.5EPZF samples at 50 °C for 30 min before (c) and after (f) grid corrosion test.

Samples	C/ wt%	O/ wt%	Zn/ wt%	F/ wt%	Si/ wt%

2.5EPZF	60.0	18.6	16.7	4.4	0.3
2.5EPZF after sunsolar irradiation	54.6	22.3	17.9	4.8	0.4
2.5EPZF at 50°C for 30min	55.0	21.9	17.4	5.2	0.5

Table 4. The EDS of samples with 2.5EPZF composite coating.

3.11. The large scale&irregular shape preparation of 2.5EPZF coating and their superhydrophobicity

The preparation of the large scale&irregular shape with the superhydrophobic 2.5EPZF coating was shown in Figure 14. In Figure 14a, the results illustrated that the spraying method to prepare the 2.5EPZF coating could complete the large area preparation and the composite 2.5EPZF coating was with the superhydrophobicity of ink, juice, milk and tea. Figure 14b indicated that the preparation of superhydrophobic coating could be assisted in rapid application to irregularly shaped substrate.

Figure. 14. Digital photos of the large scale&irregular shape samples with 2.5EPZF coating and their superhydrophobicity: (a) large scale samples with 2.5EPZF coating and the superhydrophobicity of ink, juice, milk and tea; (b) irregular shape samples with 2.5EPZF coating and the superhydrophobicity of water 2.5EPZF samples.

4. Conclusions

In this study, by one-step spray method a three-dimensional superhydrophobic 2.5EPZF composite coating was prepared. The spraying method provides a feasible solution to prepare the controllable three-dimensional structure coating. The 2.5EPZF composite coating has durable hydrophobic, good mechanical adhesion and self-cleaning, antifouling and corrosion resistance. The composite coating also has the function of repairing scratches under sunsolar irradiation and heating at 50 ^{o}C. Furthermore, the superhydrophobic large scale&irregular shape of 2.5EPZF composite coating can be prepared. The above functions have application value for the application of 2.5EPZF composite coating in marine ships.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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