Mechanically robust hydrophobic bio-based epoxy coatings for anti-corrosion application

Zheng, Shunli; Bellido-Aguilar, Daniel Angel; Huang, Yinjuan; Zeng, Xianting; Zhang, Qichun; Chen, Zhong

2019

Zheng, S., Bellido-Aguilar, D. A., Huang, Y., Zeng, X., Zhang, Q., & Chen, Z. (2019). Mechanically robust hydrophobic bio-based epoxy coatings for anti-corrosion application. *Surface and Coatings Technology*, 363, 43-50. doi:10.1016/j.surfcoat.2019.02.020

<https://hdl.handle.net/10356/142980>

<https://doi.org/10.1016/j.surfcoat.2019.02.020>

© 2019 Elsevier B.V. All rights reserved. This paper was published in *Surface and Coatings Technology* and is made available with permission of Elsevier B.V.

Downloaded on 26 Apr 2023 19:10:54 SGT

Mechanically robust hydrophobic bio-based epoxy coatings for anti-corrosion application

Shunli Zheng ^a, Daniel Angel Bellido-Aguilar ^a, Yinjuan Huang ^a, Xianting Zeng ^b, Qichun

Zhang ^a, Zhong Chen ^{a,*}

^a School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, 639798, Singapore

^b Singapore Institute of Manufacturing Technology, 2 Fusionopolis Way, Singapore 138634

Abstract: Corrosion of aluminum and its alloys causes serious problems to our daily life. As a common method for corrosion protection, epoxy resin has been widely used as the coating material due to its easy processability and excellent properties. However, its high water absorption and brittleness, as well as the usage of volatile organic solvents during coating preparation, has limited its applications in some areas. In this study, we reported an environmentally friendly hydrophobic coating based on bio-epoxy using water as the only solvent during the preparation. The coating was fabricated by introducing superhydrophobic SiO₂ nanoparticles, a hydrophobic curing agent, and hexadecyltrimethoxysilane into an isosorbide-based epoxy resin via a one-step spin coating process. The coating exhibits high hydrophobicity with a water contact angle (CA) of $134 \pm 3^\circ$. This as-prepared coating is found to have good mechanical robustness against sands erosion: it maintained a high water repellence with the CA of $146 \pm 2^\circ$ after sands erosion for 30 s. In addition, the as-obtained coating shows a one-order of magnitude reduction in the corrosion current density (J_{corr}), a positive shift of the corrosion potential (E_{corr}) from -1.008 V to -0.747 V, and an inhibition efficiency of 92%.

Keywords: Bio-based epoxy coatings, Hydrophobic, Mechanical robustness, Corrosion resistance

1. Introduction

Aluminum (Al) and its alloys are the most popular metals in modern industry owing to their advantages, such as low specific weight, high specific strength and excellent electrical conductivity. However, they are highly prone to corrosion in wet or/and salty environments [1, 2]. Various attempts have been made to enhance the corrosion resistance of the Al and its alloys. Epoxy coatings, as a common method for metal protection, have been introduced due to its prominent properties including chemical resistance, thermal stability, electrical insulating property and strong adhesion to be against aggressive environments [3, 4]. However, the applications were constrained due to the high water absorption of epoxy under humid condition and corrosive environment [5-8]. Water absorption not only deteriorates the thermal and mechanical properties for the epoxy resins, but also initiates the corrosion on Al and its alloy substrates, which could eventually lead to the delamination of the coatings [9]. Thus, it is desirable to transform the intrinsically hydrophilic property to hydrophobic by introducing hydrophobic modifier [10, 11]. Besides, the pure epoxy coatings are usually susceptible to damage of abrasion and wear, showing poor mechanical and tribological resistance [12]. Therefore, a lot of attention has been paid to the epoxy coatings with addition of nanofillers to enhance the mechanical properties [13-15].

Inspired by surface structure of lotus leave, water-repellent coatings with good hydrophobicity or superhydrophobicity whose corresponding contact angles (CAs) are higher than 90° or 150° respectively, have attracted great interest in scientific research and industrial fields due to their unique properties including anti-corrosion [16-19], self-cleaning [20-24], anti-icing [25-28], drag reduction [29, 30] and oil-water separation [31, 32]. The approaches to produce such coatings mainly involve two main aspects: low surface energy modification and rough structure construction [33, 34]. Guo et al. [35] prepared a micro-nanoscale flowerlike ZnO/epoxy resin

coating by mixing epoxy resin with its curing agent and the ZnO powders first, followed with the **modification by steric acid**. The as-obtained superhydrophobic coating showed excellent mechanical stability and high water repellence. Psarski et al. [11] produced superhydrophobic epoxy composite coatings by introducing dual-sized filler, combining surface sandblasting treatment and chemical modification of 1H,1H,2H,2H-perfluorodecyltrichlorosilane. The coatings exhibited the CA of 152° and excellent erosion wear resistance. Ramesh et al. [10] created hydrophobic epoxy/PDMS composite coatings by incorporation of ZnO nanoparticles using solution intercalation method. The results showed that the introduced nanofillers inside the coatings can improve the barrier and corrosion-resistant performances. However, these epoxy coatings were prepared using diglycidyl ether of bisphenol A (DGEBA), which is derived from bisphenol A (BPA) and epichlorohydrin [36, 37]. As is well known, BPA contributes more than 67% of the molar mass of DGEBA, and is mainly from fossil resources and proven to be harmful to human health especially on endocrine system [38, 39]. Taking into consideration of the adverse effects to human body, many countries have restricted the use of BPA in certain products, such as baby bottles and food packages. Therefore, it is urgent to explore the novel substitutes of BPA for the preparation of the new epoxy resin.

Isosorbide, transformed from glucose, is a sustainable and biodegradable material with similar structures as BPA. It is an ideal candidate for synthesis of isosorbide diglycidyl ether to replace DGEBA. Another known drawback of the conventional fossil-derived epoxy lies with the use of organic solvents in the preparation, which contain pungent or volatile compounds that cause environmental pollution and pose risks to human health. To overcome this problem, no-VOC (volatile organic compound) solvent will be ideal. Especially, the use of water as the solvent to replace VOC solvent is highly desirable. To the best of our knowledge, there has been very little

work to prepare bio-based hydrophobic epoxy coatings, especially the ones that can be processed by using water as the only solvent.

Herein, an eco-friendly hydrophobic bio-based epoxy coating was fabricated by applying a coating solution containing nanoparticles and hexadecyltrimethoxysilane (HTMS) mixed with the isosorbide based epoxy resin and hydrophobic curing agent. Water was used as the only solvent. SiO₂ nanoparticles were introduced to increase the surface roughness and mechanical property for the coatings. HTMS was used as a hydrophobic modifier to lower the surface energy. The as-prepared epoxy coating shows high water repellency with CA around 134°. Besides, the mechanical and corrosion resistance properties were evaluated.

2. Experimental

2.1 Preparation of coatings

Microscope glass slides with the size of 25 mm × 76 mm and Al foils with the size of 20 mm × 20 mm were cleaned in acetone, ethanol and DI water for 5 min respectively before drying in air. To prepare the coating, 2.4 g deionized (DI) water was added into 4 g hydrophobic curing agent Dynasylan[®] F 8815 (Evonik Industries, Germany) with magnetic stirring for 30 min. Then 0.3 g superhydrophobic SiO₂ nanoparticles (#6864HN, 99.8%, 10-25 nm, Skyspring Nanomaterials, Inc., USA) and 0.3 g hydrophobic modifier hexadecyltrimethoxysilane (HTMS, ≥ 85%, Sigma-Aldrich, USA) were added into the solution under constant stirring for another 30 min. Separately, 2 g isosorbide based epoxy was mixed with 0.8 g DI water with the same stirring time for 30 min. After that, the isosorbide based epoxy solution was mixed with the curing agent containing the nano-SiO₂ dispersion under vigorous stirring for 2 h. The final mixture was spin-coated on the cleaned glass and Al foil substrates, followed by curing at 180°C for 2 h in oven under ambient atmosphere. For comparison, bare substrate without any coating is denoted as sample #1. Coatings containing isosorbide based epoxy only, the Dynasylan[®] F 8815 only (be used as

coating alone), and epoxy with curing agent without the addition of SiO₂ nanoparticles and HTMS are denoted as #2, #3, #4, respectively, while the bio-epoxy coating with the as-received superhydrophobic nanoparticles, HTMS, and the hydrophobic curing agent is denoted as #5.

2.2 Coatings characterization

CA was measured using an OCA 20 contact angle equipment (DataPhysics Corporation, Germany) with 5 μ L water droplet. For each sample, at least 5 positions were measured to obtain the average value. The surface energy was measured with DI water, ethylene glycol and n-hexadecane following the Owens, Wendt, Rabel and Kalble (OWRK) method [40-42]. The surface morphology was observed under a field emission scanning electron microscope (FESEM, JEOL JSM-7600F, Japan). Surface roughness was measured with a surface profiler (Alpha-Step IQ Surface Profiler, KLA Tencor) with the scan length of 2000 μ m. The thermal property of the coatings was studied in N₂ atmosphere with the temperature ramped from -70 °C to 200 °C at a heating rate of 10 °C /min through differential scanning calorimetry (DSC, Q10, TA Instruments) measurement. The mechanical robustness was tested by a micro-sandblaster tester (LTH Machinery Pte Ltd, Singapore) with the sand size of 10-30 μ m. The sands were vertically blasted to the exposed coating surface under 200 kPa pressure for 30 s with a distance of 15 cm from the abrasive gun. The CA after the sands erosion was measured to evaluate the sands erosion resistance. Electrochemical measurements were carried out on an electrochemical workstation (CHI 660d, Shanghai Chenhua Instrument Corporation) using a standard three-electrode cell configuration with Ag/AgCl as the reference electrode, platinum sheet as the counter electrode, and the bare Al foil substrate and coated samples as the working electrode in 3.5 wt.% NaCl solution (pH $\approx$ 6.0) in ambient condition. The exposed area for the tested samples is 1.0 cm². Before the electrochemical tests, the samples were immersed into the corrosion medium for 1 h to obtain the stable open circuit potential (OCP). Prior to the potentiodynamic polarization curves

measurement, the electrochemical impedance spectroscopy (EIS) was performed in a frequency range of 10^{-1} to 10^5 Hz at OCP by applying a sinewave amplitude of 5 mV. The EIS results were analyzed on the basis of equivalent circuits fitted by the Zsimpwin software. The samples coated on the Al foils were only used for the electrochemical measurements.

3. Results and discussion

3.1 Wettability of coatings

The CAs for different samples were measured to evaluate the hydrophobicity, as shown in Fig. 1. It can be seen that the CAs for the bare glass substrate (#1) and isosorbide based epoxy coating (#2) are $26 \pm 2^\circ$ and $48 \pm 2^\circ$ respectively, indicating their hydrophilic nature. The sample coated with hydrophobic curing agent alone (#3) displays hydrophobicity with a CA of $111 \pm 1^\circ$. For the coating (#4) cured only with the epoxy resin and curing agent, the CA was increased a little bit to $113 \pm 2^\circ$. It is noticeable that the CA has a sharp increase ($134 \pm 3^\circ$) when the superhydrophobic SiO_2 nanoparticles and hydrophobic modifier HTMS were introduced for coating #5.

3.2 Surface morphology and surface energy of coatings

The surface morphologies of samples at different magnifications are shown in Fig. 2. Sample #4 with the epoxy and curing agent only is relatively smooth [Fig. 2(a) and (b)] while the surface for the coating #5 is rough with porous structures [Fig. 2(c) and (d)] due to the agglomeration of nanoparticles. The rough and porous structures on coating #5 allow the air to be trapped inside, which could reduce the contact area at solid-liquid interface, thus leading to a higher water repellence.

The surface roughness for the samples is shown in Fig.3. It can be seen that both the arithmetic average roughness (R_a) and root-mean-square roughness (rms, R_q) were slightly increased when the bare glass substrates were coated with isosorbide based epoxy (#2), hydrophobic curing agent (#3) and epoxy with hydrophobic curing agent (#4), while there was significant increase for

coating #5 with nano-SiO₂ inside. For the relatively smooth coating #4, although the epoxy coating was cured with the hydrophobic curing agent, it is too flat to construct a highly water repellent surface. Once the rough porous structures are introduced on the coating #5, the high hydrophobicity can be obtained due to the markedly increased roughness. As a consequence, the CA of the surface is related to the synergy of rough surface structures and low surface energy material (HTMS).

As shown in Fig. 4, there is a general trend that the higher the CA, the lower the apparent surface energy for the samples. The apparent surface energy decreased dramatically from 62.08 mJ/m² (#1) and 55.28 mJ/m² (#2) to 11.09 mJ/m² (#3) and 19.64 mJ/m² (#4) when the coating surface changes from hydrophilic to hydrophobic. For the smooth surfaces (#1 - 4), the measured surface energy of the samples is mainly determined by the content of exposed hydrophobic component on the surface. The surface energy for #4 is higher than that for #3 due to the hydrophilic epoxy in sample #4. With the addition of the nanoparticles, the surface morphology also plays an important role together with the hydrophobic component towards the measured apparent surface energy. In such cases, the increased roughness is beneficial to the reduction of the apparent surface energy. Sample #5 displayed the lowest apparent surface energy of 5.10 mJ/m² among all samples.

3.3 Thermal property

The glass transition temperature (T_g) is related to the cross-linking density in materials so as to influence the structural rigidity. The higher degree of cross-linking in microscopic scale reflects the higher T_g on a macro scale, i.e., thermally more stable in the heated state for the coating material. As shown in Fig. 5(a), the samples #3 shows the lowest $T_g \sim -29.9$ °C among all the tested coatings while the sample #2 has a much higher $T_g \sim 33.3$ °C. After the iso-epoxy was cured with the curing agent, the T_g was increased to ~ 43.8 °C for sample #4, indicating the

strong cross-linking density in the curing process. In comparison, the T_g was changed to $\sim 32.5^\circ\text{C}$ for sample #5, which can be ascribed to the negative effects of compatibility between nanoparticles and resin as well as the long alkyl chain of the HTMS. However, the T_g was still much higher than that of sample #3 and similar to that of sample #2.

To explore the thermal stability of sample #5, the influence of exposure time in ambience on the T_g was measured, as shown in Fig. 5(b). It is clear that there is no obvious change in T_g for sample #5 even after being exposed for 21 days under ambient condition, indicating its good thermal stability.

3.4 Mechanical robustness

To evaluate the mechanical robustness of the as-prepared coating #5, the micro-sandblasting test [Fig. 6(a)] was performed following the ASTM F1864 test standard to investigate the change of CA before and after the test. As seen in Fig. 6(b), the CA for the coating #5 has increased from $134 \pm 3^\circ$ to $146 \pm 2^\circ$, showing an even higher water repellence after sandblasting treatment for 30 s.

To understand the reason, the surface morphology of the coating #5 after sandblasting was investigated, and typical FESEM images are shown in Fig. 7. Comparing with Fig. 2(c) and (d), one can conclude that more porous structures with larger pore size were formed on the blasted surface, which allows more air to be entrapped beneath the water droplet. In such cases, the coating #5 can retain higher water resistance. This implies that the as-fabricated coating #5 can be highly durable against sand erosion to withstand strong physical damage.

3.4 Anti-corrosion performance

As shown in Fig. 8, all the samples have one capacitive loop. The part of the capacitive loop at high frequency (characteristic frequency $\sim 10^4$ Hz in the amplified diagram) is due to the solution resistance while the part at medium and low frequencies can be ascribed to the charge transfer

reaction at the interface of the sample surface and the corrosive medium in the electric double layer [43]. As known, the larger the diameter of the capacitive loop, the better the resistance of the coating. It is clear that the diameter of the Nyquist loop for the sample #5 is the largest among all the tested samples, indicating that the corrosion resistance has been greatly enhanced with the presence of such coating. The corresponding equivalent circuit inserted in Fig. 8 shows the same electrochemical corrosion model of R(QR) for these samples. In this circuit, R_s is the solution resistance, R_{ct} represents the charge transfer resistance and Q represents the constant phase element (CPE) of electrical double layer, which was used instead of pure capacitive to give a more accurate fitting in consideration of dispersing effect. The impedance of the CPE is mathematically expressed as:

$$Z_{CPE} = \frac{1}{Y_0} \cdot (j\omega)^{-n} \quad (1)$$

where j is the imaginary root, ω is the angular frequency, Y_0 is the magnitude and n is the exponential term which lies between 0 and 1. The capacitive loops showed the imperfect semicircles in Fig. 8 confirms the existence of dispersing effect. The fitted parameters of EIS results were summarized in Table 1. The R_{ct} value for different samples can reveal the difference in corrosion resistance. The sample #5 has a higher R_{ct} of $8.882 \times 10^6 \Omega \cdot \text{cm}^2$ as compared to the bare substrate ($3.430 \times 10^6 \Omega \cdot \text{cm}^2$) while the R_{ct} for sample #4 ($2.507 \times 10^6 \Omega \cdot \text{cm}^2$) is even lower than that of the uncoated one.

Besides, the corresponding Bode plots were also presented in Fig. 9. In Fig. 9(a), the impedance modulus at the lowest tested frequency has been commonly used as a semi-quantitative indicator for the barrier performance of the coating [44]. It can be seen that the modulus for the sample #5 at low frequency region is $4.73 \times 10^5 \Omega \cdot \text{cm}^2$, which is similar to that of sample #4 ($4.33 \times 10^5 \Omega \cdot \text{cm}^2$) and almost 2 times that of the bare Al foil #1 ($2.87 \times 10^5 \Omega \cdot \text{cm}^2$). In Fig. 9(b), the coated

surface of sample #5 shows high and wide phase angle closer to -90° in the middle and low frequency region, implying a better corrosion resistance.

Table 1. Electrochemical impedance parameters fitted from EIS results of different samples.

Samples	R_s ($\Omega \cdot \text{cm}^2$)	CPE_{dl}		R_{ct} ($\Omega \cdot \text{cm}^2$)
		$\text{CPE}-Y_{o-dl}$ ($\text{S} \cdot \text{sec}^n \cdot \text{cm}^{-2}$)	$\text{CPE}-n_{dl}$	
#1	15.00	4.231×10^{-6}	0.9203	3.430×10^6
#4	15.61	3.099×10^{-6}	0.9688	2.507×10^6
#5	15.86	2.694×10^{-6}	0.9572	8.882×10^6

The potentiodynamic polarization curves for #1, #4 and #5 were shown in Fig. 10. The corresponding corrosion potential (E_{corr}), corrosion current density (J_{corr}) and polarization resistance (R_p) obtained according to Tafel extrapolation are listed in Table 2. Usually a lower J_{corr} and a more positive E_{corr} as well as a higher R_p correspond to a better anti-corrosion performance. It can be found that the E_{corr} for the sample #5 has an obvious positive shift of 0.261 V and 0.234 V as compared to that for the sample #1 and sample #4, respectively. Comparing with sample #1 ($6.068 \times 10^{-8} \text{ A} \cdot \text{cm}^{-2}$), the J_{corr} of sample #5 ($4.739 \times 10^{-9} \text{ A} \cdot \text{cm}^{-2}$) was reduced by 1 order of magnitude while there is no considerable reduction for sample #4 ($1.683 \times 10^{-8} \text{ A} \cdot \text{cm}^{-2}$). Besides, sample #5 displays a much higher R_p , which is 7 times higher than that of sample #1 and 5 times bigger than that of sample #4, suggesting its excellent potential to protect bare Al foil substrate against corrosion. The corresponding corrosion inhibition efficiency η_p for the samples can be estimated using the following equation [45]:

$$\eta_p(\%) = \frac{J_{corr}^0 - J_{corr}}{J_{corr}^0} \times 100 \quad (2)$$

where the J_{corr} and J_{corr}^0 are the corrosion current density for the coated and uncoated samples, respectively. Sample #5 showed a η_p of 92%, which is much higher than that of sample #4 (72%), furthering confirming its higher corrosion protection performance for the bare substrate.

Summarizing the findings mentioned above, it can be found that the potentiodynamic polarization curves agrees very well with the results obtained from the Nyquist and Bode plots. All results indicate that the highly hydrophobic coating #5 possesses much improved corrosion resistance for the bare Al foil substrates.

Fig. 11 shows the EIS spectra and potentiodynamic polarization curves of sample #5 obtained during long-term immersion in 3.5 wt.% NaCl solution. Sample #5 demonstrated high capacitive behavior with only slightly decreased diameter in the capacitive loop in Nyquist plots [Fig. 11(a)]. The Bode impedance plots [Fig. 11(b)] and Bode phase plots [Fig. 11(c)] are almost identical over 7-day immersion period. The barrier performance for bare Al foil substrate changed little despite a small negative shift in E_{corr} from -0.747 V to -0.783 V. However, the η_p still kept a high value of 89% [Fig. 11(d)] and Table 2].

Table 2. Electrochemical parameters of potentiodynamic polarization curves and corresponding inhibition efficiency for different samples.

Samples	E_{corr} (V vs. Ag/AgCl)	J_{corr} ($\text{A}\cdot\text{cm}^{-2}$)	R_p ($\Omega\cdot\text{cm}^2$)	Inhibition efficiency (η_p %)
#1	-1.008	6.068×10^{-8}	7.854×10^5	—
#4	-0.981	1.683×10^{-8}	1.071×10^6	72
#5 (0 day)	-0.747	4.739×10^{-9}	5.718×10^6	92
#5 (7 days)	-0.783	6.504×10^{-9}	5.908×10^6	89

According to the above results, it can be deduced that the anti-corrosion mechanism for the coatings is attributed to the contact modes between corrosive solution and coating surfaces, as shown in Fig. 12. For the rough coating of sample #5 [Fig. 12(b)], the surface covered with rough porous structures can trap air inside to form a layer of “air cushion”. Therefore, the liquid-solid contact area, i.e., the area between NaCl solution and coating surface was reduced drastically as

compared to that for the flat coating of sample #4 [Fig. 12(a)], so that the corrosive ions (Cl^-) are more effectively prevented from reaching the bare substrate [46].

4. Conclusions

In this study, a green bio-based epoxy coating was successfully developed using a simple spin-coating method by introducing the nanoparticles and hydrophobic modifier into the epoxy matrix. The coating shows hydrophobicity with a CA of $134 \pm 3^\circ$, and is able to maintain high water repellence after sands erosion, indicating its good mechanical robustness. Meanwhile, the electrochemical measurement results indicated that this hydrophobic coating owns more positive E_{corr} , smaller J_{corr} , higher R_{ct} as well as better inhibition efficiency, demonstrating the improved corrosion resistance. The designed hydrophobic epoxy coating exhibiting enhanced mechanical strength holds good promising potential for corrosion-resistant applications on various engineering substrates.

Acknowledgements

The authors would like to thank the Agency for Science, Technology and Research (A*STAR) of Singapore (SERC 1528000048) for funding.

References

- [1] S. Sharifi Golru, M.M. Attar, B. Ramezanzadeh, Effects of surface treatment of aluminium alloy 1050 on the adhesion and anticorrosion properties of the epoxy coating, *Appl. Surf. Sci.* 345 (2015) 360-368.
- [2] W.A. Badawy, F.M. Al-Kharafi, A.S. El-Azab, Electrochemical behaviour and corrosion inhibition of Al, Al-6061 and Al-Cu in neutral aqueous solutions, *Corros. Sci.* 41 (1999) 709-727.
- [3] M. Cui, S. Ren, H. Zhao, Q. Xue, L. Wang, Polydopamine coated graphene oxide for anticorrosive reinforcement of water-borne epoxy coating, *Chem. Eng. J.* 335 (2017) 255-266.
- [4] M. Chrysanthos, J. Galy, J.-P. Pascault, Preparation and properties of bio-based epoxy networks derived from isosorbide diglycidyl ether, *Polymer* 52 (2011) 3611-3620.
- [5] J. Tan, W. Liu, Z. Wang, Hydrophobic epoxy resins modified by low concentrations of comb-shaped fluorinated reactive modifier, *Prog. Org. Coat.* 105 (2017) 353-361.

- [6] S. Gubanski, R. Hartings, Swedish research on the application of composite insulators in outdoor insulation, *IEEE Electr. Insul. Mag.* 11 (1995) 24-31.
- [7] S. Kumagai, W. Xinsheng, N. Yoshimura, Surface degradation phenomena of outdoor polymer insulating materials due to acid rain, *IEEJ Trans. Fund. Mater.* 116 (1996) 1121-1128.
- [8] C. Zhou, X. Lu, Z. Xin, J. Liu, Y. Zhang, Hydrophobic benzoxazine-cured epoxy coatings for corrosion protection, *Prog. Org. Coat.* 76 (2013) 1178-1183.
- [9] S.-Y. Zhang, Y.-F. Ding, S.-J. Li, X.-W. Luo, W.-F. Zhou, Effect of polymeric structure on the corrosion protection of epoxy coatings, *Corros. Sci.* 44 (2002) 861-869.
- [10] S. Ammar, K. Ramesh, B. Vengadaesvaran, S. Ramesh, A. Arof, Amelioration of anticorrosion and hydrophobic properties of epoxy/PDMS composite coatings containing nano ZnO particles, *Prog. Org. Coat.* 92 (2016) 54-65.
- [11] M. Psarski, G. Celichowski, J. Marczak, K. Gumowski, G.B. Sobieraj, Superhydrophobic dual-sized filler epoxy composite coatings, *Surf. Coat. Technol.* 225 (2013) 66-74.
- [12] B. Wetzel, F. Hauptert, M. Qiu Zhang, Epoxy nanocomposites with high mechanical and tribological performance, *Compos. Sci. Technol.* 63 (2003) 2055-2067.
- [13] S. Ammar, K. Ramesh, I.A.W. Ma, Z. Farah, B. Vengadaesvaran, S. Ramesh, A.K. Arof, Studies on SiO₂-hybrid polymeric nanocomposite coatings with superior corrosion protection and hydrophobicity, *Surf. Coat. Technol.* 324 (2017) 536-545.
- [14] S. Palraj, M. Selvaraj, K. Maruthan, G. Rajagopal, Corrosion and wear resistance behavior of nano-silica epoxy composite coatings, *Prog. Org. Coat.* 81 (2015) 132-139.
- [15] M. Conradi, A. Kocijan, D. Kek-Merl, M. Zorko, I. Verpoest, Mechanical and anticorrosion properties of nanosilica-filled epoxy-resin composite coatings, *Appl. Surf. Sci.* 292 (2014) 432-437.
- [16] S. Zheng, C. Li, Q. Fu, M. Li, W. Hu, Q. Wang, M. Du, X. Liu, Z. Chen, Fabrication of self-cleaning superhydrophobic surface on aluminum alloys with excellent corrosion resistance, *Surf. Coat. Technol.* 276 (2015) 341-348.
- [17] T. Xiang, S. Zheng, M. Zhang, H.R. Sadig, C. Li, Bio-inspired slippery zinc phosphate coating for sustainable corrosion protection, *ACS Sustainable Chem. Eng.* 6 (2018) 10960-10968.
- [18] S. Peng, X. Yang, D. Tian, W. Deng, Chemically stable and mechanically durable superamphiphobic aluminum surface with a micro/nanoscale binary structure, *ACS Appl. Mater. Interfaces* 6 (2014) 15188-15197.
- [19] W. Xu, J. Song, J. Sun, Y. Lu, Z. Yu, Rapid fabrication of large-area, corrosion-resistant superhydrophobic Mg alloy surfaces, *ACS Appl. Mater. Interfaces* 3 (2011) 4404-4414.
- [20] M. Zhong, Y. Zhang, X. Li, X. Wu, Facile fabrication of durable superhydrophobic silica/epoxy resin coatings with compatible transparency and stability, *Surf. Coat. Technol.* 347 (2018) 191-198.

- [21] Y. Qing, C. Hu, C. Yang, K. An, F. Tang, J. Tan, C. Liu, Rough structure of electrodeposition as a template for an ultrarobust self-cleaning surface, *ACS Appl. Mater. Interfaces* 9 (2017) 16571-16580.
- [22] S. Wang, X. Yu, Y. Zhang, Large-scale fabrication of translucent, stretchable and durable superhydrophobic composite films, *J. Mater. Chem. A* 5 (2017) 23489-23496.
- [23] S. Zheng, C. Li, Q. Fu, W. Hu, T. Xiang, Q. Wang, M. Du, X. Liu, Z. Chen, Development of stable superhydrophobic coatings on aluminum surface for corrosion-resistant, self-cleaning, and anti-icing applications, *Mater. Des.* 93 (2016) 261-270.
- [24] Y. Lu, S. Sathasivam, J. Song, C.R. Crick, C.J. Carmalt, I.P. Parkin, Robust self-cleaning surfaces that function when exposed to either air or oil, *Science* 347 (2015) 1132-1135.
- [25] S. Zheng, C. Li, Q. Fu, T. Xiang, W. Hu, J. Wang, S. Ding, P. Liu, Z. Chen, Fabrication of a micro-nanostructured superhydrophobic aluminum surface with excellent corrosion resistance and anti-icing performance, *RSC Adv.* 6 (2016) 79389-79400.
- [26] Y. Shen, G. Wang, J. Tao, C. Zhu, S. Liu, M. Jin, Y. Xie, Z. Chen, Anti-icing performance of superhydrophobic texture surfaces depending on reference environments, *Adv. Mater. Interfaces* 4 (2017) 1700836.
- [27] X. W, Z. Chen, A Mechanically robust transparent coating for anti-icing and self-cleaning applications, *J. Mater. Chem. A* 6 (2018) 16043-16052.
- [28] L. Wang, Q. Gong, S. Zhan, L. Jiang, Y. Zheng, Robust anti-icing performance of a flexible superhydrophobic surface, *Adv. Mater.* 28 (2016) 7729-7735.
- [29] H. Dong, M. Cheng, Y. Zhang, H. Wei, F. Shi, Extraordinary drag-reducing effect of a superhydrophobic coating on a macroscopic model ship at high speed, *J. Mater. Chem. A* 1 (2013) 5886-5891.
- [30] S. Srinivasan, W. Choi, K.-C. Park, S.S. Chhatre, R.E. Cohen, G.H. McKinley, Drag reduction for viscous laminar flow on spray-coated non-wetting surfaces, *Soft Matter* 9 (2013) 5691-5702.
- [31] S. Gao, X. Dong, J. Huang, S. Li, Y. Li, Z. Chen, Y. Lai, Rational construction of highly transparent superhydrophobic coatings based on a non-particle, fluorine-free and water-rich system for versatile oil-water separation, *Chem. Eng. J.* 333 (2018) 621-629.
- [32] Y. Lu, S. Sathasivam, J. Song, F. Chen, W. Xu, C.J. Carmalt, I.P. Parkin, Creating superhydrophobic mild steel surfaces for water proofing and oil–water separation, *J. Mater. Chem. A* 2 (2014) 11628-11634.
- [33] D. Kumar, L. Li, Z. Chen, Mechanically robust polyvinylidene fluoride (PVDF) based superhydrophobic coatings for self-cleaning applications, *Prog. Org. Coat.* 101 (2016) 385-390.
- [34] A.K. Sasmal, C. Mondal, A.K. Sinha, S.S. Gauri, J. Pal, T. Aditya, M. Ganguly, S. Dey, T. Pal, Fabrication of superhydrophobic copper surface on various substrates for roll-off, self-cleaning, and water/oil separation, *ACS Appl. Mater. Interfaces* 6 (2014) 22034-22043.

- [35] X. Zhang, Y. Si, J. Mo, Z. Guo, Robust micro-nanoscale flowerlike ZnO/epoxy resin superhydrophobic coating with rapid healing ability, *Chem. Eng. J.* 313 (2017) 1152-1159.
- [36] J. Wan, B. Gan, C. Li, J. Molina-Aldareguia, E.N. Kalali, X. Wang, D.-Y. Wang, A sustainable, eugenol-derived epoxy resin with high biobased content, modulus, hardness and low flammability: synthesis, curing kinetics and structure-property relationship, *Chem. Eng. J.* 284 (2016) 1080-1093.
- [37] J.-M. Raquez, M. Deléglise, M.-F. Lacrampe, P. Krawczak, Thermosetting (bio)materials derived from renewable resources: a critical review, *Prog. Polym. Sci.* 35 (2010) 487-509.
- [38] S. Ma, X. Liu, Y. Jiang, Z. Tang, C. Zhang, J. Zhu, Bio-based epoxy resin from itaconic acid and its thermosets cured with anhydride and comonomers, *Green Chem.* 15 (2013) 245-254.
- [39] J. Łukaszczuk, B. Janicki, M. Kaczmarek, Synthesis and properties of isosorbide based epoxy resin, *Eur. Polym. J.* 47 (2011) 1601-1606.
- [40] D.K. Owens, R. Wendt, Estimation of the surface free energy of polymers, *J. Appl. Polym. Sci.* 13 (1969) 1741-1747.
- [41] W. Rabel, Einige aspekte der benetzungstheorie und ihre anwendung auf die untersuchung und veränderung der oberflächeneigenschaften von polymeren, *Farbe und Lack* 77 (1971) 997-1006.
- [42] D. Kaelble, Dispersion-polar surface tension properties of organic solids, *J. Adhesion* 2 (1970) 66-81.
- [43] Z. Song, Z. Xie, L. Ding, Y. Zhang, Corrosion resistance of super-hydrophobic coating on AZ31B Mg alloy, *Int. J. Electrochem. Sci.* 13 (2018) 6190-6200.
- [44] G. Bierwagen, D. Tallman, J. Li, L. He, C. Jeffcoate, EIS studies of coated metals in accelerated exposure, *Prog. Org. Coat.* 46 (2003) 149-158.
- [45] M. Behpour, S.M. Ghoreishi, M. Salavati-Niasari, B. Ebrahimi, Evaluating two new synthesized S–N Schiff bases on the corrosion of copper in 15% hydrochloric acid, *Mater. Chem. Phys.* 107 (2008) 153-157.
- [46] T. Liu, S. Chen, S. Cheng, J. Tian, X. Chang, Y. Yin, Corrosion behavior of super-hydrophobic surface on copper in seawater, *Electrochim. Acta* 52 (2007) 8003-8007.

Figure captions:

Fig. 1. CA of different samples.

Fig. 2. FESEM images of samples at different magnifications: (a)-(b) #4; (c)-(d) #5.

Fig. 3. Surface roughness of different samples.

Fig. 4. Measured apparent surface energy of different samples.

Fig. 5. (a) T_g of different coatings; (b) T_g of sample #5 after exposure to ambient condition for different time.

Fig. 6. (a) Schematic of the micro-sandblasting equipment; (b) CA of sample #5 before and after sandblasting for 30 s.

Fig. 7. FESEM images of sample #5 at different magnifications after sandblasting for 30 s.

Fig. 8. The Nyquist plots of different samples in 3.5 wt.% NaCl solution. The insets are the amplified diagram in the high frequency range and the corresponding equivalent circuit of the samples.

Fig. 9. The Bode plots of different samples in 3.5 wt.% NaCl solution.

Fig. 10. The potentiodynamic polarization curves for different samples measured in 3.5 wt.% NaCl solution.

Fig. 11. Sample #5 after immersion in 3.5 wt.% NaCl solution for 7 days: (a) Nyquist plots; (b) Bode impedance plots; (c) Bode phase plots; (d) potentiodynamic polarization curves.

Fig. 12. Contact modes between corrosive solution and coating surface: (a) #4; (b) #5.

Figure 1
[Click here to download high resolution image](#)

Figure 1

Figure 2
[Click here to download high resolution image](#)

Figure 2

Figure 3
[Click here to download high resolution image](#)

Figure 3

Figure 4

[Click here to download high resolution image](#)

Figure 4

Figure 5
[Click here to download high resolution image](#)

Figure 5

Figure 6
[Click here to download high resolution image](#)

Figure 6

Figure 7

Figure 8
[Click here to download high resolution image](#)

Figure 8

Figure 9
[Click here to download high resolution image](#)

Figure 9

Figure 10

[Click here to download high resolution image](#)

Figure 10

Figure 11
[Click here to download high resolution image](#)

Figure 11

Figure 12

Natural resource of glucose

Isosorbide

- Derived from glucose
- Non-toxic diol produced from bio-based feedstocks
- Biodegradable and thermally stable
- Low price

Bio-based epoxy