Communications in Physics, Vol. 33, No. 4 (2023), pp. 447-455
DOI: https://doi.org/10.15625/0868-3166/18506

Evaluation of the hydrophobic and barrier properties of the polyurethane coatings covered by stearic acid thin layer

Thuy Duong Nguyen[1,2], **Thu Thuy Pham**[1], **Ke Oanh Vu**[1], **Thi Xuan Hang To**[1,2],
Trinh Lan Phuong[2], **Xuan Thang Dam**[3], **Minh Quy Bui**[4] **and Anh Son Nguyen**[1,2,†]

[1] *Institute for Tropical Technology, Vietnam Academy of Science and Technology,*
18 Hoang Quoc Viet, Cau Giay, Hanoi, Vietnam

[2] *Graduate University of Science and Technology, Vietnam Academy of Science and Technology,*
18 Hoang Quoc Viet, Cau Giay, Hanoi, Vietnam

[3] *Faculty of Chemical Technology, Hanoi University of Industry,*
298 Cau Dien street, Hanoi, Vietnam

[4] *Faculty of Chemistry, Thai Nguyen University of Sciences, Thai Nguyen, Vietnam*

E-mail: [†]nason@itt.vast.vn

Received 18 April 2023; *Accepted for publication 15 July 2023*; *Published 13 December 2023*

Abstract. *In this paper, a thin stearic acid (SA) film was deposited onto the polyurethane (PU) coatings with different concentrations of stearic acid in the ethanol (1 wt.%, 2 wt.% and 3 wt.%) by centrifuged technique. Fourier transform infrared spectra (FTIR) and water contact angle (WCA) method were performed to characterize and evaluate the hydrophobic layer formed on the surface of the samples. Then, the barrier property of the PU/SA was assessed by using electrochemical impedance spectroscopy (EIS) and accelerated salt spray test method. The results show that the presence of the stearic acid layer was effective for both hydrophobic and barrier properties, especially the samples prepared with 3 wt.% stearic acid. This work landmarks the need for improving the protection ability of polyurethane coatings for a metallic substrate.*

Keywords: stearic acid film; polyurethane; hydrophobicity; barrier property.
Classification numbers: 81.40.Pq; 81.65.Kn; 82.45.Kn.

1. Introduction

Due to high mechanical strength and inexpensiveness, steel has been one of the popular materials for outdoor construction [1]. However, steel is severely degraded when exposed to outdoor environments, especially marine and industrial environments [2]. To prolong the life of steel, various effective methods have been studied and applied to enhance corrosion protection, such as: organic/inorganic coatings and cathodic protection [3, 4]. Organic coatings such as epoxy, polyurethane, and acrylic coatings prevail in use to prolong the life of steel due to their low cost. Organic coatings have acted as a physical barrier, which prevented the steel surface to be exposed to corrosive media [5, 6].

Electrochemical impedance spectroscopy (EIS) is a popular non-destructive technique to evaluate the shielding ability of organic coatings [7, 8]. The shielding ability of organic coatings significantly affects the impedance response of metallic surface/coatings systems when small amplitude alternating voltage signals are applied [3, 7]. Cai et al. assessed the barrier ability of PU coatings without and with addition of CeO_2 nanoparticles on AA7075 substrate by using EIS [9]. The low-frequency impedance (Z_{10mHz}) reduced obviously and two semicircles were observed from Nyquist plot after one cycle of aging tests, confirming that the water molecules and aggressive ions penetrated through the PU coatings and led to decreased shielding ability of PU coatings [9]. Li et al. also used EIS to study the durability of waterborne polyurethane (WPU) coatings containing Ce-MMT nanocomposite on carbon steel [10]. The authors indicated that the WPU coatings with higher impedance value had good shielding ability, which limited the entry of aggressive species from the environment into the substrate [10].

During exposure of sample to a corrosive media, water molecules penetration into the organic coating can decrease adhesion of coatings, which can be detrimental to corrosion resistance of substrates. Water contact angle (WCA) test is used for the hydrophobic property of organic coatings [11]. Xiao et al. and Ye et al. investigated the hydrophobicity of epoxy coatings by WCA, their results suggested that the coatings with better hydrophobicity also had higher $Z_{0.01Hz}$ values [12, 13]. It indicated that the hydrophobicity of coatings can significantly influence their barrier property as well as mechanical strength.

To improve the hydrophobicity of the organic coatings without modifying their structure, hydrophobic-enhanced organic coatings have been studied and developed. Stearic acid (SA, $CH_3(CH_2)_{16}COOH$) is a biocompatible and environmentally friendly natural saturated fatty acid with a hydrophobic methyl group [14]. Previous studies successfully prepared surfaces with hydrophobic organic coating by using stearic acid solutions [15]. Penna et al. prepared stearic acid modified with alumina nanoparticles as a top layer onto bottom epoxy coatings [15]. WCA results indicated that the stearic acid coating exhibited superhydrophobic properties and low interactions with water droplets at the surface [15].

In this work, the shielding ability and hydrophobicity of PU coating were improved by a thin stearic acid layer. The appearance of stearic acid coating on surface of PU coating was investigated by Fourier-transform infrared (FT-IR). The WCA test was used to evaluate the hydrophobicity of their PU coatings. The shielding ability of PU coatings without and with stearic acid layer was investigated by EIS and salt sprays tests.

2. Experiment

2.1. Materials

Stearic acid (95%) from Sigma Aldrich was used to make thin film. The used polyurethane coating was a bicomponent system obtained from Nippon Polyurethane Industry. The resin is polyacrylate (ACRYDIC AC-3596-AR, Thailand) with a solid content of about 70 wt.% and the OH value in the solid function is 55-65 mgKOH/g. The polyisocyanate-based hardener (CORONATE-HX, Japan) is solvent-free (solid content > 99.4 wt.%) with an NCO content of about 20.5 - 22%.

2.2. *Preparation of polyurethane coatings*

For preparation of coating systems, carbon steel samples with dimensions of 10 × 15 × 0.2 cm were used. The surface of samples was polished with abrasive papers 400 grades then cleaned and dried. Then, the polyurethane coatings were applied to steel plates by a spin coating method at 300 rpm in 30 second. These coatings were dried in 72 hours at ambient condition before being applied a thin film of stearic acid. The thickness of dried PU coatings was $40 \pm 3 \mu m$ (measured by using the Minitest 600, Sheen).

2.3. *Fabrication of polyurethane/ stearic acid coating*

Due to the low solubility, the A solution of stearic acid at 3 concentrations in ethanol (1, 2, and 3 weight %) was prepared at ambient condition. The thin stearic acid layer on PU covered steel plates was formed by spin-coating method (speed of 1000 rpm in 30 seconds) as described in Fig. 1. The PU coatings with SA layer formed at SA concentrations of 1 wt.%, 2 wt.% and 3 wt.% were named PU/SA1, PU/SA2 and PU/SA3. The thickness of the stearic thin film was negligible compared with the thickness of the original PU coating. The stearic acid film did not change the thickness of the PU coating.

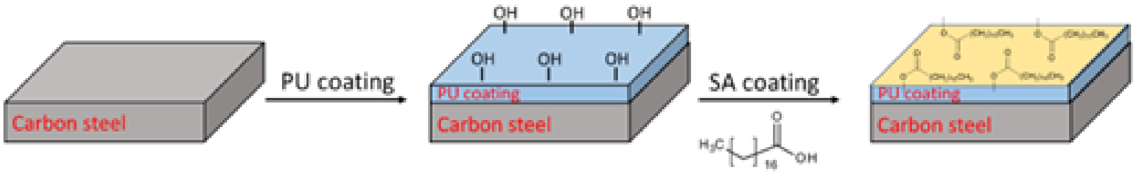


Fig. 1. Preparation process of the recovered PU coating by stearic acid.

2.4. *Analytical methods*

Fourier transform infrared spectra (FTIR) of the pure PU coating and the stearic thin film covered PU coatings with different concentrations were measured on Nexus 670 Nicolet spectrometer with resolution at 32 cm^{-1} using Attenuated Total Reflectance (ATR) mode. The spectra were obtained in the region of 600 - 4000 cm^{-1}.

The wetting angle of the samples was determined on an OCA 50 Dataphysics instrument (Germany) by a sessile drop according to the diameter and height of a drop of distilled water with a volume of 5 μL applied to the sample.

The barrier properties of coating samples were examined by electrochemical impedance test with a Biologic SP300. The impedance spectra of the coatings were measured by a 3-electrode system: coated steel as working electrode, saturated calomel (SCE) as reference electrode and platinum grid as counter electrode. The samples were glued by cylindrical PVC pipes containing 3% NaCl electrolyte solution. The contact area of the sample surface with the aggressive medium was 28 cm^2. The electrochemical impedance test was done with a frequency interval from 100 kHz to 10 mHz. For each coating system, three samples were done.

PU samples with stearic thin films were tested in a Q-FOG CCT-600 chamber according to ASTM B117. The exposure time was 168 hrs. For each coating system, three samples were tested.

3. Results and discussion

FTIR spectra was used to determine the presence of the hydrophobic layer onto the polyurethane coating. While water contact angle test, electrochemical impedance spectroscopy and the salt-spray test were performed to study the effect of the stearic acid layer on the barrier properties of the organic coating system.

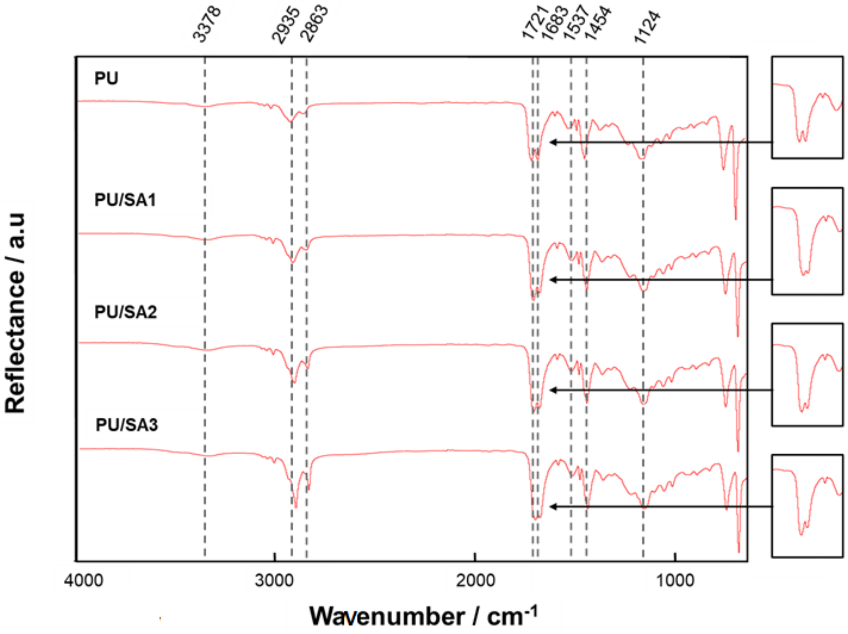


Fig. 2. FTIR spectrum of PU with and without stearic acid (indicated in the figure).

Figure 2 shows the FTIR spectra of PU coatings with and without treatment by stearic acid solution at different concentrations. The spectrum of pure PU displayed the peaks at 3378 cm^{-1} and 1721 cm^{-1} corresponding to the stretching of C=O stretching vibration of the carboxyl group. The peaks at 2935 cm^{-1}, 2863 cm^{-1} and 1454 cm^{-1} represent the asymmetric, symmetric stretching and the scissoring vibrations of -CH$_2$ in the PU matrix, respectively [16, 17]. The peak at 1683 cm^{-1}, 1537 cm^{-1} and 1124 cm^{-1} can be correlated to the stretching vibration of C=N, C=O and C-N bond, respectively [18]. For the PU/SA coating samples with the presence of stearic acid on the surface, all the characteristics peaks of PU are also observed. This result is explained by the negligible thickness of the stearic layer deposited on the PU coatings. Because the concentrations of the stearic acid in ethanol solution were very dilute, 1-3 wt.%, that could be introduced only a very thin layer of stearic and the spectrum of FTIR technique can show both characteristics peaks of stearic acid and PU coating. Besides, stearic acid is a fatty acid with -CH and -COOH groups that were also represented in the FTIR spectrum at these peaks around 2935 cm^{-1}, 2863 cm^{-1} and 1721 cm^{-1}, respectively [17]. The spectra of the coatings containing SA show that the intensity of the peak at 1683 cm^{-1} decreases with the increase of the stearic acid concentration, compared to the intensity of the peak at 1721 cm^{-1}. It can be due to the presence of stearic acid on the surface of the PU coating, which leads to an increase in the ratio between the C=O bond (represented in the structure of both polyurethane and stearic acid) and the C=N bond (represented in the structure of only polyurethane). Moreover, the peak at around 1537 cm^{-1} can be seen on the spectra of all samples, but for the PU containing SA, it has been slightly shifted, compared to pure PU. These changes can be attributed to the interaction of C=O groups between the stearic acid and the polyurethane coating.

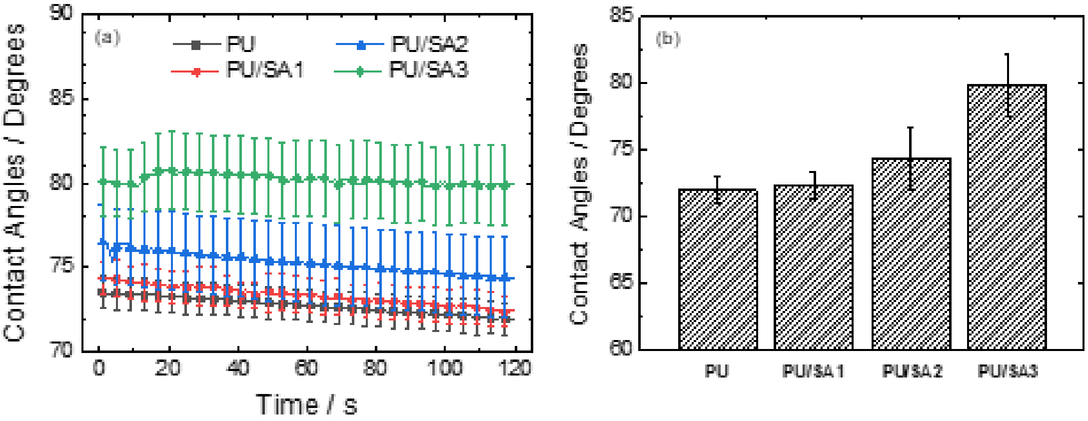
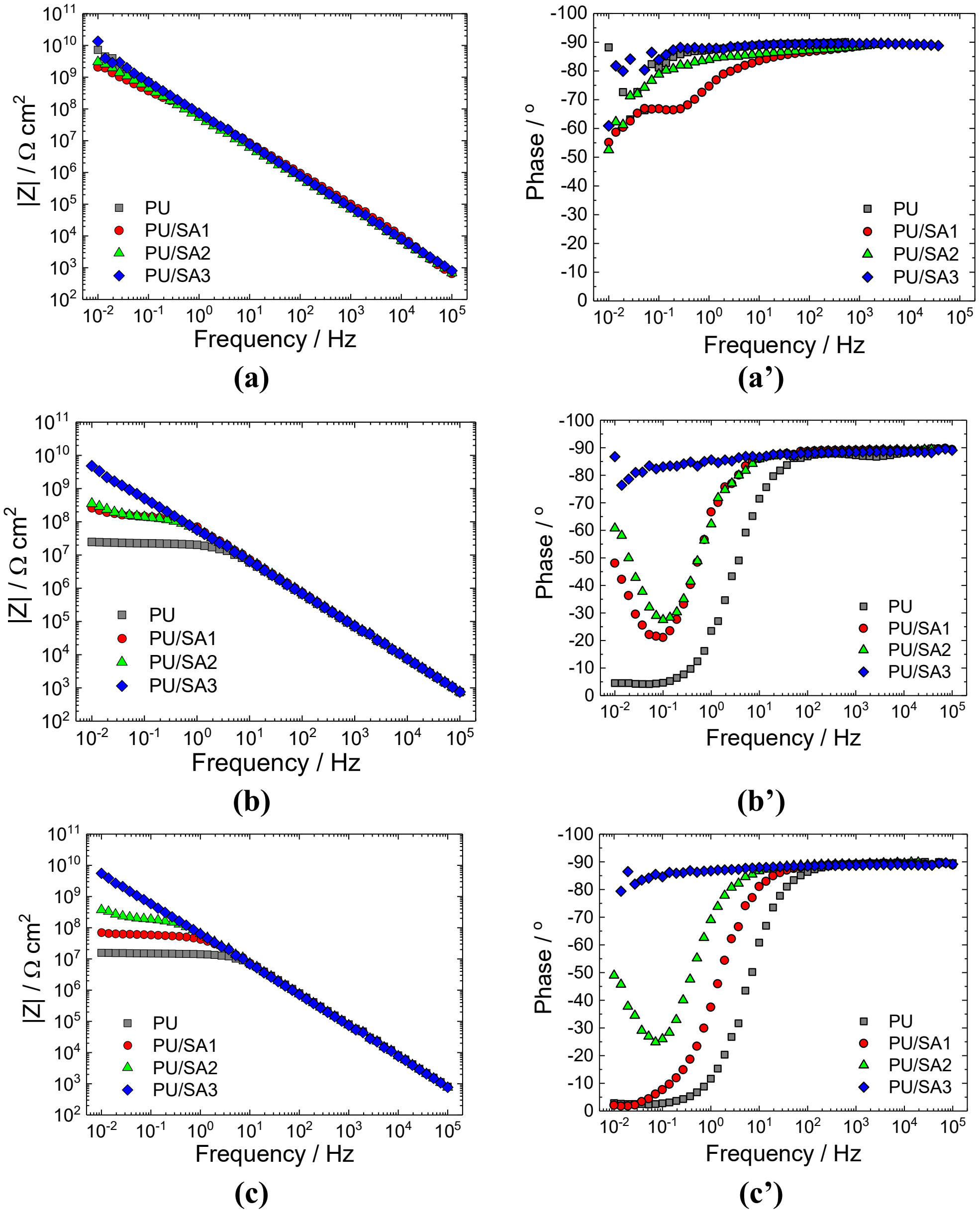


Fig. 3. Contact angles of PU, PU/SA1, PU/SA2 and PU/SA3 as a function of time (a) and after 120 seconds tested (b).

The presence of the top thin SA layer had affected the wettability of polyurethane surface. The hydrophobic character of PU coatings with and without treatment was illustrated by water contact angle (WCA) measurements. The WCA values of tested coatings are shown in Fig. 3. The coatings with SA layer on the surface exhibited better hydrophobic ability than the PU coating. Fig. 3(a) displays the WCA values of the coatings as a function of the water droplet contacted time. The pure PU coating represented the smallest WCA values at the beginning of the test (73.5°) that decreased with the exposed time (72.0° after 120 seconds). While the coatings treated with 1 wt.% and 2 wt.% of the SA solution have a better hydrophobic character than the pure PU coating (74.4° and 76.5° at the beginning, respectively), but they displayed a decrease in the WCA values as a function of exposed time. For the PU coating treated with 3 wt.% of the SA solution, the WCA value of this sample was almost stable throughout the WCA measurement, 80.0°. After 120 seconds, the PU/SA3 illustrated the best WCA value. Meanwhile, the hydrophobic property of the PU/SA1 and PU/SA2 was slightly better than the pure PU coating (Fig. 3(b)). The results can be explained by the formation of the stearate layer on the surface of the PU coating, which represents a hydrophobic character. And the higher the concentration of SA solution treatment used, the greater the number of hydrophobic groups presented on the surface of the PU coating (PU/SA3 > PU/SA2 > PU/SA1 > PU).

Because of the formation of the thin hydrophobic layer on the surface, the properties barrier of PU coatings was enhanced. Fig. 4 shows the EIS spectra of PU with and without treatment by stearic acid solution after 1 day, 4 weeks and 8 weeks of the immersion in the 3 wt.% NaCl solution. In the first day of immersion time (Fig. 4(a) and 4(a')), the Bode plots disclosed a



(a) (a’)

(b) (b’)

(c) (c’)

Fig. 4. Impedance diagrams of PU, PU/SA1, PU/SA2 and PU/SA3 (indicated into the figures) obtained after a day (a, a’), 4 weeks (b, b’) and 8 weeks (c, c’) immersed in a 3 wt.% NaCl solution.

remarkably larger impedance modulus value (from 3.10^{9} Ωcm^{2} to 1.10^{10} Ωcm^{2}), and the phase angle remained from 80^{o} to 89^{o} at high frequency for all samples. These results can be explained by a good barrier property that prevented the penetration of the electrolyte throughout the coatings. However, for the PU/SA coating, at the low frequency, it formed a second time constant with 65^{o}

of phase angle, that is due to the slight diffusion of the electrolyte into the coatings. After 4 weeks exposed, the Bode phase angle diagram clearly showed one time constant (the phase value obtained at the low frequency range was close to 0^o), and the impedance values of PU without treatment significantly decreased, around 3.10^7 Ωcm^2, correspond to the resistance of PU coating (Fig. 4(b) and 4(b')). This phenomenon can be explained by the complete penetration of the electrolyte solution into the PU coating, and the corrosion phenomenon began to process. For the PU/SA1 and PU/SA2, their impedance values also decreased after 4 weeks of immersion time, and they presented two time constant. However, these values remain still high, 4.10^8 Ωcm^2 with the phase angle of 20^o and 30^o corresponding to PU/SA1 and PU/SA2, respectively, at low frequency. It can be attributed to the presence of the hydrophobic layer on the surface, and no corrosion product was observed. Fig. 4(c) and 4(c') illustrate the electrolyte penetration phenomena into the coatings after 8 weeks immersed in the NaCl solution. It evidently represents the difference between the coatings treated with the stearic acid solution at different concentrations. After this period, only PU/SA3 had a very high impedance value, 6.10^9 Ωcm^2 and represented only one time constant. It had approximately unchanging from the beginning. For the PU/SA2 coating, the impedance value has slightly decreased, but it remains higher than the other coatings, except for PU/SA3. Meanwhile, the impedance value of the PU/SA1 coatings decreased close to untreated PU, it exhibits a worse barrier property of PU/SA1 than that of PU/SA2 and PU/SA3. After 8 weeks of exposure in a 0.5 M NaCl solution, it can be concluded that the presence of a hydrophobic layer on the surface of the coatings can improve the barrier properties. This layer was denser, the barrier property of the coatings was better, PU/SA3 > PU/SA2> PU/SA1 > PU.

The barrier property of the coatings was also evaluated by using the salt spray test. For this aim, the sample was placed into the test chamber without artificial scratches. Fig. 5 presents the optical photographs of the PU coatings with and without SA treatment after 168 hours performed in the salt-spray chamber. It can easily observe the corrosion production on the surface of non-treatment PU coating. For the PU/SA1 coating, there was a corrosion phenomenon, but it did not mark compared to non-treatment PU. On the other hand, after 168 hours exposed in the salt-spray chamber, there were no corrosion products or swelling points observed on the surface of the PU/SA2 and PU/SA3 coatings. The results confirm that the SA hydrophobic layer can prevent not only the penetration of electrolyte solution, but also the diffusion of moisture and Cl^- into the tested coatings. The results showed good agreement with the WCA and EIS measurements.

4. Conclusion

PU coatings were covered with a thin hydrophobic organic layer by dipped in the stearic acid (SA) solution with different concentrations. With the presence of SA film, the WCA value of treated PU coatings was greater than the PU coatings without treatment. From 2 wt.% concentration of SA treatment solution, the effect of the hydrophobic layer showed remarkable. The PU/SA3 showed the greatest WCA value and was stable during the WCA measurement. Moreover, with high hydrophobic effect on the surface, the PU/SA3 coatings also provided a great barrier property. It can prevent the penetration of the electrolyte containing corrosion agent after 4 weeks of immersion time and the moisture with the concentrated Cl^- ions after 168 hours of exposure in salt-spray chamber. This work proposes a facile method to enhance the protection of the organic coatings against the corrosion of the metal substrate.

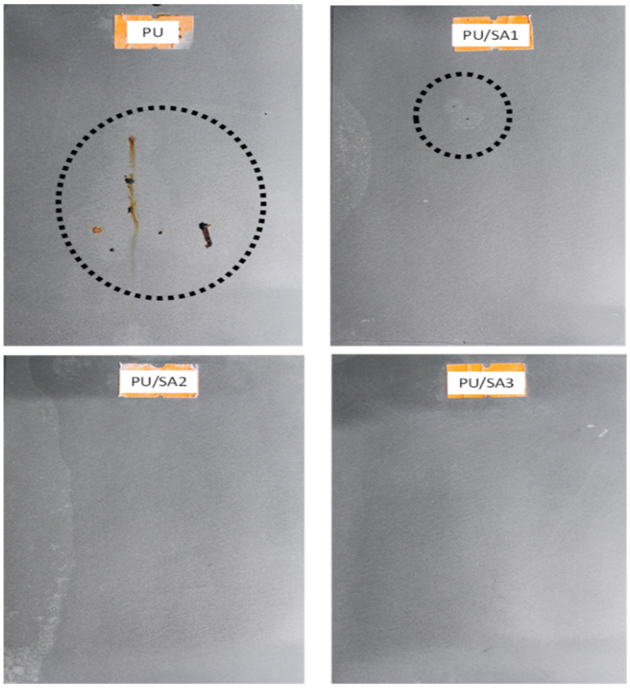


Fig. 5. Optical photographs of PU, PU/SA1, PU/SA2 and PU/SA3 after 168 hours tested in the salt-spray chamber.

Acknowledgments

The authors gratefully acknowledge the financial support of the Vietnam Academy of Science and Technology under the project number TDVLTT.04/21-23.

References

[1] Q. A. Jawad, D. S. Zinad, R. D. Salim, A. A Al-Amiery, T. S. Gaaz, M. S. Takriff and A. A. H. Kadhum, *Synthesis, Characterization, and Corrosion Inhibition Potential of Novel Thiosemicarbazone on Mild Steel in Sulfuric Acid Environment*, Coatings **9** (11) (2019) 729.

[2] J. Alcantara, D. Fuente, B. Chico, J. Simancas, I. Diaz and M. Morcillo, *Marine Atmospheric Corrosion of Carbon Steel: A Review*, Materials (Basel) **10** (3) (2017) 406.

[3] T. D. Nguyen, A. S. Nguyen, B. A. Tran, K. O. Vu, D. L. Tran, T. T. Phan, N. Scharnagl, M. L. Zheludkevich and T. X. H. To, *Molybdate intercalated hydrotalcite/graphene oxide composite as corrosion inhibitor for carbon steel*, Surf. Coat. Technol. **399** (2020) 126165.

[4] C. Wang, W. Gao, N. Liu, Y. Xin, X. Liu, X. Wang, Y. Tian, X. Chen and B. Hou, *Covalent organic framework decorated TiO_2 nanotube arrays for photoelectrochemical cathodic protection of steel*, Corros. Sci. **176** (2020) 108920.

[5] T. A. Truc, T. T. Thuy, V. K. Oanh, T. T. X. Hang, A. S. Nguyen, N. Caussé and N. Pébère, *8-hydroxyquinoline-modified clay incorporated in an epoxy coating for the corrosion protection of carbon steel*, Surf. Interfaces **14** (2019) 26.

[6] T. T. X. Hang, N. T. Dung, T. A. Truc, N. T. Duong, B. V. Truoc, P. G. Vu, T. Hoang, D. T. M. Thanh, M. -G. Olivier, *Effect of silane modified nano ZnO on UV degradation of polyurethane coatings*, Prog. Org. Coat. **79** (2015) 68.

[7] P. Haghdadeh, M. Ghaffari, B. Ramezanzadeh, G. Bahlakeh and M. R. Saeb, *Polyurethane coatings reinforced with 3-(triethoxysilyl)propyl isocyanate functionalized graphene oxide nanosheets: Mechanical and anti-corrosion properties*, Prog. Org. Coat. **136** (2019) 105243.

[8] I. C. P. Margarit-Mattos, *EIS and organic coatings performance: Revisiting some key points*, Electrochim. Acta **354** (2020) 136725.

[9] G. Cai, S. Xiao, C. Deng, D. Jiang, X. Zhang and Z. Dong, *CeO_2 grafted carbon nanotube via polydopamine wrapping to enhance corrosion barrier of polyurethane coating*, Corros. Sci. **178** (2021) 109014.

[10] S. Li, S. Wang, X. Du, H. Wang, X. Cheng and Z. Du, *Waterborne polyurethane coating based on tannic acid functionalized Ce-MMT nanocomposites for the corrosion protection of carbon steel*, Prog. Org. Coat. **163** (2022) 106613.

[11] R. Abakah, F. Huang, Q. Hu, Y. Wang and J. Liu, *Comparative study of corrosion properties of different graphene nanoplate/epoxy composite coatings for enhanced surface barrier protection*, Coatings **11** (3) (2021) 285.

[12] X. Xiao, Z. Ye, G. Meng and L. Gu, *Mussel-inspired preparation of superhydrophobic mica nanosheets for long-term anticorrosion and self-healing performance of epoxy coatings*, Prog. Org. Coat. **178** (2023) 107456.

[13] Y. Ye, D. Yang, D. Zhang, H. Chen, H. Zhao, X. Li and L. Wang, *POSS-tetraaniline modified graphene for active corrosion protection of epoxy-based organic coating*, Chem. Eng. J **383** (2020) 123160.

[14] W. Zhang, Y. Chen, M. Chen, S. Zhao, J. Mao, A. Qu, W. Li, Y. Zhao, N. Huang and G. Wan, *Strengthened corrosion control of poly (lactic acid) (PLA) and poly (ε-caprolactone) (PCL) polymer-coated magnesium by imbedded hydrophobic stearic acid (SA) thin layer*, Corros. Sci. **112** (2016) 327.

[15] M. O. Penna, A. A. Silva, F. F. do Rosário, S. De Souza Camargo and B. G. Soares, *Organophilic nano-alumina for superhydrophobic epoxy coatings*, Mater. Chem. Phys. **255** (2020) 123543.

[16] O. R. Pardini and J. I. Amalvy, *FTIR, ^{1}H-NMR spectra, and thermal characterization of water-based polyurethane/acrylic hybrids*, J. Appl. Polym. Sci. **107** (2) (2008) 1207.

[17] H. Huang, M. Tian, J. Yang, H. Li, W. Liang, L. Zhang and X. Li, *Stearic acid surface modifying Mg(OH)2: Mechanism and its effect on properties of ethylene vinyl acetate/$Mg(OH)_2$ composites*, J. Appl. Polym. Sci. **107 (5)** (2008) 3325.

[18] Y. Liu, J. Ma, T. Wu, X. Wang, G. Huang, Y. Liu, H. Qiu, Y. Li, W. Wang, and Jianping Gao, *Cost-effective reduced graphene oxide-coated polyurethane sponge as a highly efficient and reusable oil-absorbent*, ACS Appl. Mater. Interfaces **20 (5)** (2013) 10018.