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Formation and characterization of organic silicon and fluoropolymers film on epoxy base for corrosion protection of carbon steel

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Abstract. Coating systems using epoxy resin, organic silicon compounds (octadecyltrichlorosilane (OTS) and hydrolyzed heptadecafluoro tetrahydro decyltrimethoxysilane (HDFS)), and fluoropolymers (polytetrafluoroethylene (PTFE), and polyvinylidene fluoride (PVDF)), were applied to carbon steel. Epoxy (EP) coating and EP/OTS, EP/HDFS systems were produced via spin coating, while PTFE and PVDF layers were deposited using electron beam dispersion. Wettability, surface structure, and tribological properties were assessed through contact angle measurement, Fourier transform infrared reflection (FTIR), and tribotechnical test. Anticorrosion resistance was evaluated using electrochemical techniques, salt spray, and adhesion tests. Surface modifications with silicon compounds and fluoropolymers increased hydrophobicity, anticorrosion behavior and wear resistance. The water contact angles of EP, EP/OTS, EP/HDFS, EP/PVDF, and EP/PTFE were 84°, 108º, 116º, 96º, and 128º, respectively. Coating treatments reduced the friction coefficient. No corrosion was observed on treated surfaces after 336 hours in a salt spray chamber, while untreated EP showed rust after 96 hours. The hydrophobic systems based on epoxy resin, silicon compounds, and fluoropolymers are effective for protecting metal structures, with fluoropolymers providing higher protection to silicon compounds.

Keywords: epoxy coatings, octadecyltrichlorosilane, heptadecafluoro tetrahydro decyltrimethoxysilane, polytetrafluoroethylene, polyvinylidene fluoride, hydrophobicity.

Classification numbers: 2.5.2, 2.5.3, 2.9.3

1. INTRODUCTION

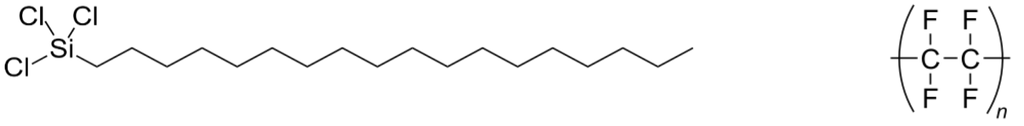
Composite materials based on epoxy resins are widely used as anticorrosive coatings due to high adhesion to carbon steel, heat resistance, low shrinkage during curing, and other properties [1]. However, polymerized epoxy coatings (EPs) are hydrophilic and highly brittle, which limits their use [2]. Therefore, they are hydrophobized to expand the application areas of EPs [1, 2]. Hydrophobization is carried out, as a rule, by adding fillers that affect the morphology and roughness of the epoxy (EP), and/or changing its chemical composition by introducing acrylates [3], amines [4, 5], siloxanes [1, 6], polyesters [7, 8], polysulfones [9] and fluorinated substances [10]. Hydrophobization of the surface of anticorrosion coatings is an urgent task of materials science and also allows expanding the scope of their application [11]. Among current surface engineering methods, pulsed laser deposition and ion sputtering have lower control and reproducibility than other methods [12]. Vacuum plasma-chemical methods that allow the formation of layers that increase the hydrophobicity of the surface based on polymers such as polytetrafluoroethylene, polyvinylidene fluoride, and other fluoropolymers are also being actively improved [12]. The technological methods used are based on the processes of creating an active gas phase containing atoms and molecular fragments capable of polymerization and chemical interaction, formed as a result of the action of a concentrated energy flow (ions, electrons, laser radiation, etc.) on the polymer in a vacuum. The processes of dispersion, transfer in the gas phase, adsorption, and physicochemical interaction are characterized by the high chemical activity of the fragments, and the introduction of filler vapor into their composition makes it possible to form composite layers of nanometer thickness of almost any composition. Among the most common methods for forming an active gas phase, one can distinguish dispersion methods under the influence of electron-beam, laser, ion-beam, high-frequency magnetron or synchrotron radiation, as well as thermal decomposition, etc. [12]. Obtaining coatings from the gas phase formed by dispersing the initial polymer has a number of advantages over the known methods of monomer polymerization from this phase. First of all, using this method, it is possible to apply thin coatings with high-performance properties at a thickness of up to 500 nm. In this case, there are no fundamental difficulties in forming coatings from almost any polymers [12]. An important technological advantage of electron-beam dispersion is the high rate of coating growth (up to 50 nm/s), which makes it possible to continuously apply fluoroplastic layers from the active gas phase [12]. In turn, to obtain epoxy (EP) and coating of organic silicon compounds, it is advisable to use the spin coating method, which is more attractive for obtaining thin films for several reasons: it is inexpensive, safer, the process is carried out at a relatively low temperature, there is no need to use metal catalysts. The coating process's controllability and reproducibility are some of this technology's main advantages [11].

In the present study, epoxy base coated with the fluoropolymers (polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF)) layer from the gas phase formed by electron beam of their dispersion or organic silicon compounds (octadecyltrichlorosilane (OTS), hydrolyzed heptadecafluoro tetrahydro decyltrimethoxysilane (HDFS)) (Figure 1) by spin coating method. The structure, wetting, and tribological properties of coating systems were investigated by FTIR, contact angle, and tribotechnical test. The anticorrosion behavior of these coatings was examined in sodium chloride solution using electrochemical impedance spectroscopy (EIS), salt spray test, and adhesion test.

2. MATERIALS AND METHODS

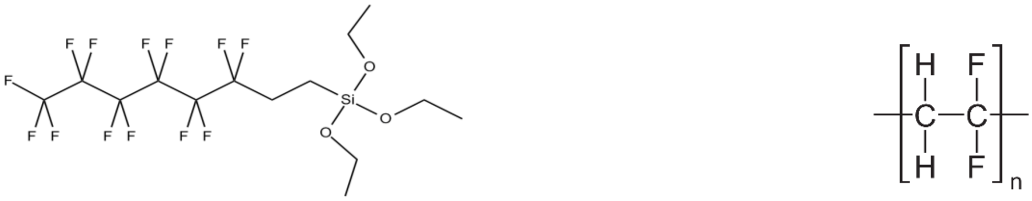
2.1. Materials

Fluoropolymers (polytetrafluoroethylene and polyvinylidene fluoride), organic silicon compounds (octadecyltrichlorosilane and hydrolyzed heptadecafluoro tetrahydro decyltrimethoxysilane), and solvents from Aldrich were used without further purification. The epoxy resin with an equivalent weight of about 460-490 g/eq (YD-011X75) and hardener-polyamide amine with an equivalent weight of active H of about 266 g/eq (307D-60) were obtained from Kukdo Chemical Co., Ltd (Korea).



Octadecyltrichlorosilane (OTS)

Polytetrafluoroethylene (PTFE)



Hydrolyzed heptadecafluoro tetrahydro decyltrimethoxysilane (HDFS)

Polyvinylidene fluoride (PVDF)

Figure 1. Chemical structure of fluoropolymers and silicon compounds.

2.2. Preparation of coating systems

2.2.1. Preparation of epoxy coatings

The epoxy/amine ratio was the stoichiometric ratio for the preparation of epoxy coating. The carbon steel sample dimension of 4 × 6 × 0.2 cm was used. The steel samples were abraded with abrasive papers 400 grades, washed with distilled water and ethanol, and then dried. The epoxy coatings were applied to steel plates using the spin coating method. The spin speed was 600 rpm, and the rotating time was 1 min. The thickness of dried EP was 30 ± 3 µm.

2.2.2. Preparation of organic silicon coatings

Hydrolysis of HDFS was carried out in isopropyl alcohol in the presence of a 25 % aqueous ammonia solution. Then, hydrolyzed HDFS was dried at a pressure of 10 mm Hg for 3 hours and dissolved in perfluorobenzene. OTS and HDFS coatings on EP surface obtained on steel plates were formed by the spin coating method. A solution of hydrolyzed HDFS in perfluorobenzene or OTS in hexane was applied to the substrates and centrifuged at a speed of 3000 rpm for 2 minutes using a high-speed centrifuge (Belarus). The masses of OTS and HDFS adsorbed on EP, estimated by the gravimetric method, were 7 g/m^2 and 4 g/m^2, respectively. The thickness of organic silicon layers was approximately calculated at about 1 - 2 µm.

2.2.3. Preparation of fluoropolymer coatings

The deposition of PTFE and PVDF coatings on steel substrates with EP was carried out from the active gas phase formed by electron beam dispersion of the corresponding target (fluoropolymer). The target was dispersed by an electron beam with an energy of 800 - 1600 eV and a current density of 0.01 - 0.03 A/cm^2. Coating was carried out at an initial pressure of residual gases in a vacuum chamber of about 4 × 10^{-3} Pa. The average distance from the electron gun to the target was 150 mm, and from the target to the steel substrate with EP, 200 mm. The thickness of thin-film fluoropolymers coating was controlled by a quartz thickness gauge and amounted to 150 nm.

2.3. Surface characterization

2.3.1. Measurement of contact angle

A DSA 100E instrument (Kruss, Germany) was used with a sessile drop method to find the contact wetting angle of the samples. The diameter and height of a 3 μl drop of distilled water were used to measure the contact angle. All measurements were made in an ambient atmosphere at room temperature.

2.3.2. Fourier transform infrared reflection spectroscopy

Fourier transform infrared reflection (FTIR) spectra of coating systems were recorded on Nexus 670 Nicolet spectrometer (Attenuated Total Reflectance (ATR) mode) in the range between 600 - 4000 cm^{-1} with a resolution of 32 cm^{-1}.

2.3.3. Electrochemical impedance test

The corrosion resistance of coating samples was examined by an electrochemical impedance test with a Biologic SP300. A three-electrode system consisting of coated steel as the working electrode, saturated calomel (SCE) as the reference electrode, and platinum grid as the counter electrode was used for measuring. The electrochemical impedance test was done with a frequency interval from 100 kHz to 10 mHz, and the 3 % NaCl solution was used as a corrosion medium. Three samples were used for each coating system.

2.3.4. Salt spray test

Samples were tested in a Q-FOG CCT-600 chamber according to ASTM B117. The 5 % NaCl solution was used for testing. Samples were exposed for 336 h, and each coating type was tested with 3 samples to evaluate repeatability.

2.3.5. Adhesion test

Samples were tested with Elcometer according to D3359. After the salt spray test, the adhesion of coating samples was determined. A grid with 25 cells was scratched on the sample's surface, and then tape was used to stick and tear. Count the number of peeling cells and calculate the percentage of peeling. Evaluate the test results as indicated in ASTM D3359, method B.

2.3.6. Tribotechnical tests

Tribological tests of coatings in a sphere-plane friction pair made of 95X18 steel – XC 35 steel were respectively carried out on a microtribometer “RPT-02” of a reciprocating type, which recorded the change in the friction coefficient (k_f) of the steel indenter along the sample depending on the number of sliding cycles [12]. Test conditions: applied load 1 N; indenter - steel ball with a diameter of 3 mm; the indenter stroke length of 3 and 6 mm in one direction and in a cycle (in forward and reverse directions), respectively; the linear speed of the indenter is 4 mm/s. The boundary conditions for experimenting on tribological damage to steel surfaces are friction coefficients of 0.47 - 0.6 [1].

3. RESULTS AND DISCUSSION

3.1. Structure characterization of coatings

3.1.1. Hydrophobicity of coatings

Figure 2 presents the water contact angle of epoxy EP, epoxy/octadecyltrichlorosilane (EP/OTS), epoxy/hydrolyzed heptadecafluoro tetrahydro decyltrimethoxysilane (EP/HDFS), epoxy/polytetrafluoroethylene (EP/PTFE), and epoxy/polyvinylidene fluoride (EP/PVDF) coatings. The results obtained are 84°, 108º, 116º, 96º, and 128º corresponding to EP, EP/OTS, EP/HDFS, EP/PVDF, and EP/PTFE samples, respectively. The presence of hydrocarbon chains in OTS molecules and fluorocarbon chains in HDFS oligomers and fluorocarbon groups in fluoropolymers increase the hydrophobicity of the EP [11, 12, 13]. The water contact angle is directly related to the surface energy and depends on surface morphology and chemical functional groups present on the surface. The PTFE and HDFS oligomershave more C–F chemical bonds in molecules and provide higher hydrophobicity than the OTS and PVDF layers (Figure 1). The molecules of PTFE and HDFS oligomers have no pronounced hydrophilic part.

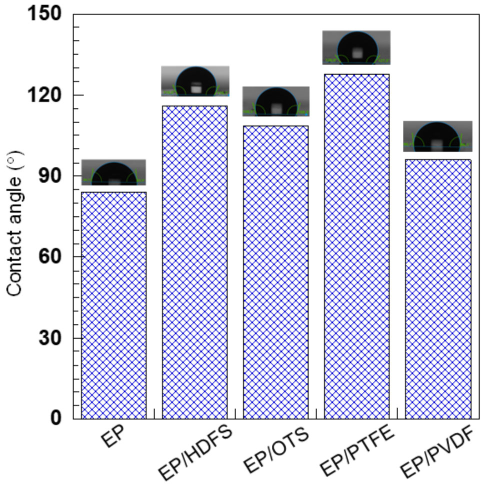


Figure 2. Contact angle of the EP, EP/HDFS, EP/OTS, EP/PTFE, and EP/PVDF coatings.

3.1.2. FTIR characterizations

Structures of coating systems were analyzed by FTIR spectroscopy. Figure 3 shows the FTIR spectra of coatings, and the characteristic bands are shown in Table 1.

For the spectrum of epoxy (EP): the major characteristic band at 3341 cm^{-1} is a significant indication of N-H group, those at 2924 cm^{-1} and 2846 cm^{-1} are attributed to hydrocarbon groups CH, and that at 1235 cm^{-1} corresponds to C-O ether group [14].

Compared with the pure epoxy coating, some new peaks appeared in the spectra of the epoxy/hydrolyzed heptadecafluoro tetrahydro decyltrimethoxysilane (EP/HDFS) and epoxy/octadecyltrichlorosilane (EP/OTS). In the spectrum of EP/HDFS coating, the peak at 2962 cm^{-1} belongs to the $Si-CH_3$ group [15]. The band around 1037 cm^{-1} corresponds to the Si-O bond [15]. The characteristic band of Si-C can be observed around 1211 cm^{-1} [15]. The peaks from 1148 to 1211 cm^{-1} and 657 cm^{-1} are attributed to the C-F group [15]. For the FTIR spectrum of EP/OTS, the bands at 2964 cm^{-1} are attributed to $Si-CH_2$ group and have quite large intensity compared to the spectrum of the pure EP [15].

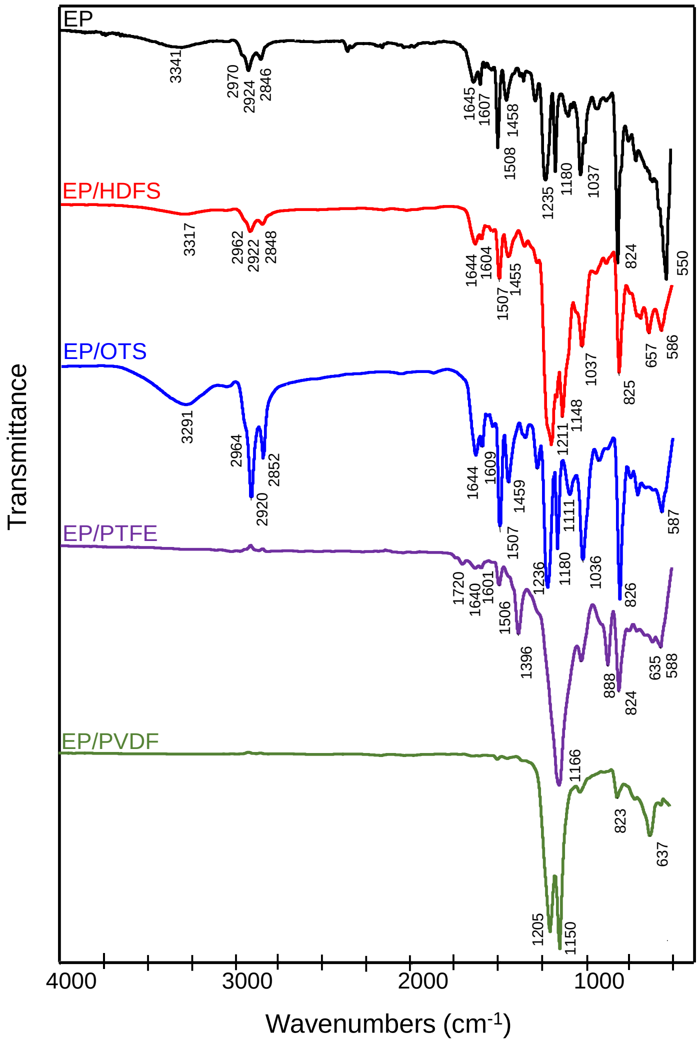


Figure 3. FTIR spectra of EP, EP/HDFS, EP/OTS, EP/PTFE, and EP/PVDF coatings.

For two fluoropolymer-treated epoxy samples (epoxy/polytetrafluoroethylene (EP/PFTE) and epoxy/polyvinylidene fluoride (EP/PVDF)), the characteristic peaks of EP appear quite small in the infrared spectrum. In the spectrum of EP/PFTE, besides the relatively small characteristic peaks for the EP coating around 1640 and 1396 cm^{-1}, it also appears as a peak at 1166 and 635 cm^{-1} belonging to -CF2 [16]. Similarly, for the spectrum of EP/PVDF sample, the characteristic peaks of PVDF at 1205, 1150, 823, and 637 cm^{-1} are due to -CF2 [17]. Hence, the characteristic peaks of EP cannot be observed on this spectrum.

These results indicate the formation of silicon compounds (HDFS and OTS) and fluoropolymer (PTFE and PVDF) layers on the EP surface, in which fluoropolymer layers cover almost the EP surface. This finding is in accordance with contact angle measurements; the structure of PTFE and HDFS compounds contains more C-F groups; this is a hydrophobic group, leading to a higher contact angle than other samples.

Table 1. Characteristic bands of FTIR spectra of EP, EP/HDFS, EP/OTS, EP/PTFE and EP/PVDF.

EP (cm^{-1})	EP/HDFS (cm^{-1})	EP/OTS (cm^{-1})	EP/PTFE (cm^{-1})	EP/PVDF (cm^{-1})	Bonds (cm^{-1})
3341	3317	3291			N-H
2970					CH aromatic
	2962	2964			Si-CH_3; Si-CH_2
2924	2922	2920			-CH_2
2846	2848	2852			-CH_3
1645	1644	1644	1720,1640		-CO amide
1607	1604	1609	1601		C-C aromatic
1508	1507	1507	1506		p-substituted benzene
1458	1455	1459	1396		-CH_2
1235	1211	1236			C-O ether bridge
	1211				Si-C
	1211-1148		1166	1205, 1150	-CF_2
1180	1148	1180	1166	1150	C-O secondary alcohol
1037	1037	1036			C-O aromatic
	1037	1111; 1036			Si-O
824	825	826	888, 824	823	out of plane bending of aromatic C-H
	657		635	637	CF_2 wagging
550	586	587	588		out of plane ring C-C bend

3.2. Corrosion resistance of coating systems

3.2.1. Electrochemical impedance spectroscopy

Figure 4 presents the impedance diagrams of epoxy (EP), epoxy/octadecyltrichlorosilane (EP/OTS), epoxy/hydrolyzed heptadecafluoro tetrahydro decyltrimethoxysilane (EP/HDFS), epoxy/polytetrafluoroethylene (EP/PTFE), and epoxy/polyvinylidene fluoride (EP/PVDF) samples obtained during immersion in 3 % NaCl solution.

It can be observed that the impedance spectra of samples are very different. After 1 day of immersion, the impedance diagram of the EP sample has two loops, indicating that the electrolyte has penetrated the metal surface and that corrosion has occurred. Meanwhile, after the first day, the EP samples modified with organic silicon compounds and fluoropolymers exhibited a strong barrier effect by presenting only one large capacitive arc. The impedance modulus at the low frequency ($|Z|_{100mHz}$) has been used as a semi-quantitative indicator of coating's barrier performance in Bode plots. The impedance modulus of all samples modified with organic silicon compounds and fluoropolymers was higher than that of the EP pure sample. The impedance modulus of the EP sample modified with PTFE was the highest compared to the surface-modified EP samples. The other three samples had similar values with limited differences.

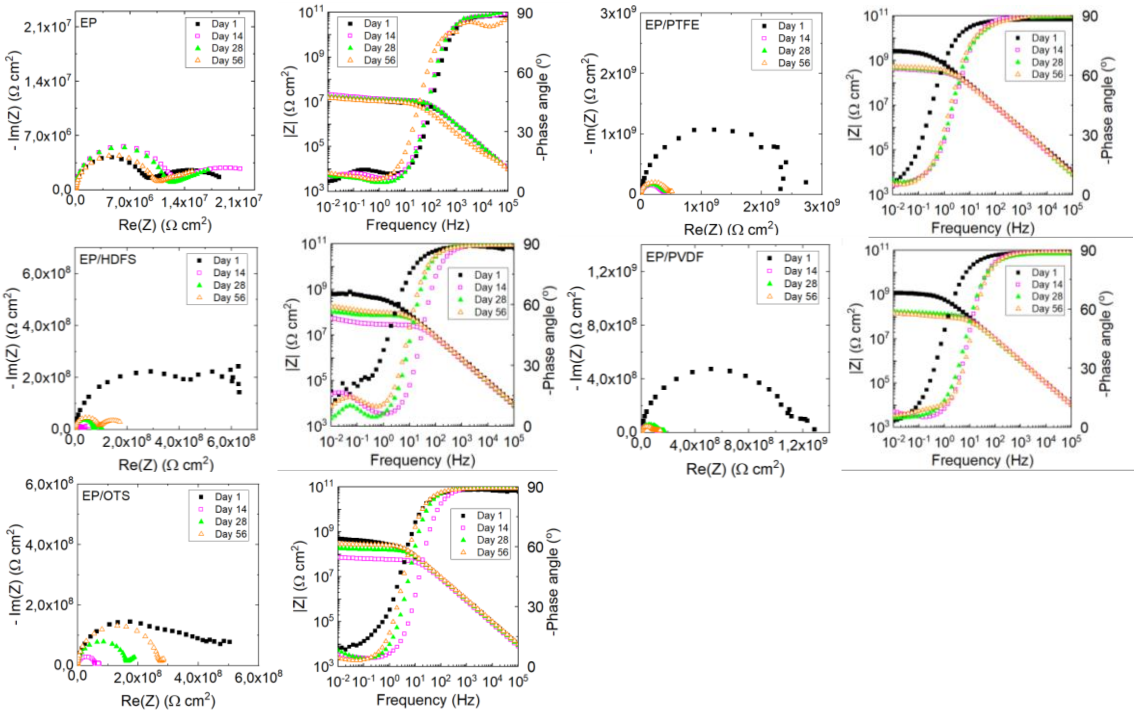


Figure 4. Electrochemical impedance diagrams obtained after immersion in 3 % NaCl solution for EP, EP/HDFS, EP/OTS, EP/PTFE, and EP/PVDF samples.

As the testing time continued to increase, after 14 days, 28 days, and 56 days of immersion in 3 % NaCl solution, the same results were obtained for the EP samples. After 14 days of testing, the electrolyte solution penetrated through the coating, leading to a decreased capacitive arc diameter. The impedance modulus value begins to decrease slightly in the Bode plots, and the phase angles also decrease at low frequencies. For the EP/HDFS sample, the impedance spectrum also began to appear a second arc (Nyquist plots) and the impedance modulus value decreased more than 10 times and the phase diagrams (Bode plots) are characteristic with two times constants, indicating a decrease in the barrier properties. It can be observed the same phenomenon for the EP/OTS and EP/PVDF samples; the second arc also begins to appear in the impedance spectrum (Nyquist plot), but the two times constants are not clearly observed in the phase diagrams (Bode plot), which indicates that the electrolyte has penetrated to the metal surface and that corrosion has occurred. Besides, the impedance modulus value decreased more than 10 times after 14 days of testing. For the EP/PTFE sample, the impedance spectrum still only appears in 1 arc (Nyquist plot) and with a constant time (Bode plot) after 14 days of testing. The impedance modulus value of the EP/PTFE sample is the highest among the samples. When the test time increased to 28 and 56 days, the EP samples modified with silicon compounds (EP/HDFS and EP/OTS) slightly increased impedance value and reached more than $10^8 \Omega.cm^2$ after 56 days of testing. Besides, the surface-modified EP samples with fluoropolymers have impedance values that do not change and remain at approximately 10^9 Ω.cm^2 for the EP/PTFE sample and more than 10^8 Ω.cm^2 for the EP/PVDF sample after 56 days of testing. The barrier properties remained consistently good after 56 days of testing. The EP sample has the lowest total impedance value after 56 days of testing, about 10^7 Ω.cm^2. All EP samples treated with fluoropolymer act as capacitors with good barrier properties.

From the impedance spectrum, the parameters of film resistance (R_f) and total impedance modulus at 100 mHz ($Z_{100\ mHz}$) and constant phase element (CPE) were determined to evaluate the deterioration process of the paint film. The parameters were calculated according to the equivalent circuit diagram in Figure 5 and Table 2. Here, R_s is the solution resistance. R_f and CPE_f represent the coating's resistance and constant phase element.

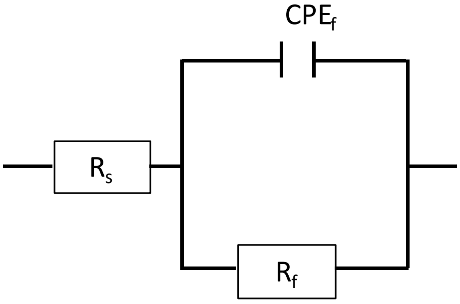


Figure 5. Electrical equivalent circuits usedto fit EIS spectra.

Table 2. Electrochemical parameters fitted from EIS results of coatings in immersion tests.

Sample	**Immersion time (day)**	**CPE$_f$ ($\Omega^{-1}.s^n.cm^{-2}$)**	**n_f**	**R_f ($\Omega.cm^2$)**	**$\|Z\|_{100mHz}$ ($\Omega.cm^2$)**
EP	1	1.79E-10	0.9873	1.04E+07	1.52E+07
EP	14	1.86E-10	0.9865	1.10E+07	1.70E+07
EP	28	1.82E-10	0.9882	1.08E+07	1.42E+07
EP	56	1.23E-09	0.8573	1.09E+07	1.23E+07
HDFS	1	2.27E-10	0.9711	4.72E+08	6.00E+08
HDFS	14	1.90E-10	1	2.80E+07	3.57E+07
HDFS	28	1.93E-10	1	6.97E+07	8.27E+07
HDFS	56	2.01E-10	0.9916	9.24E+07	1.17E+08
OTS	1	2.01E-10	0.9876	1.64E+08	4.07E+08
OTS	14	1.95E-10	1	5.88E+07	6.56E+07
OTS	28	1.76E-10	1	1.57E+08	1.67E+08
OTS	56	1.77E-10	0.992	2.61E+08	2.73E+08
PTFE	1	2.20E-10	0.9705	2.54E+09	2.14E+09
PTFE	14	1.77E-10	1	4.00E+08	3.72E+08
PTFE	28	1.79E-10	1	4.50E+08	4.14E+08
PTFE	56	1.79E-10	1	5.40E+08	4.67E+08
PVDF	1	1.74E-10	0.9896	1.18E+09	1.06E+09
PVDF	14	1.73E-10	0.9913	1.27E+08	1.75E+08
PVDF	28	1.70E-10	1	1.06E+08	1.39E+08
PVDF	56	1.74E-10	0.9913	1.10E+08	1.19E+08

Film resistance is a parameter that characterizes the ability to protect coatings under the effects of aggressive environments. Figure 6 shows the film resistance of coating samples during immersion time in 3 % NaCl solution. Film resistance is the resistance created by the electrolyte seeping into the pores of the paint film, thereby giving information about the porosity of the film. The graph shows that at the initial time, after 1 day of testing, the film resistance R_f of the EP samples modified with silicon compounds and fluoropolymers was higher than that of EP coating. These results show that the presence of silicon and fluoropolymer compounds on the surface of the EP coating significantly increased the shielding ability of the paint film. As the test time increased, the film resistance of the EP sample modified surface with silicon compounds and fluoropolymers decreased but wasstill much higher than that of the pure EP sample and very stable during testing time. Typically, coatings applied to metal surfaces often have defects that prevent the coating from being completely tight. When immersed in an aggressive environment, the electrolyte will diffuse into the film along these defects, causing metal corrosion and causing adecrease in the film resistance of the coatings during the exposure time. After 56 days of testing, the film resistance values of all samples with modified surfaces were about 10^8 Ω.cm^2 and higher than that of the pure EP sample. Among the studied samples, the EP/PTFE sample has the highest film resistance, followed by the EP/OTS sample and the other 2 samples. These results show that the presence of these compounds has significantly increased the shielding ability of the EP coating.

To evaluate the corrosion resistance of samples, impedance modulus at a frequency of 100 mHz ($Z_{100\ \mathrm{mHz}}$) was extracted from impedance diagrams. The variations of $Z_{100\ \mathrm{mHz}}$ of samples during tests are shown in Figure 6. For the impedance module value at 100 mHz, the exact change as with the film resistance of coatings was realized. It is observed that after 14 days of immersion of $Z_{100\ \mathrm{mHz}}$, the value of all samples decreased slightly. The decrease in $Z_{100\ \mathrm{mHz}}$ value indicates degradation of coatings due to the penetration of electrolytes into the pores of the coating. As the test time increased, the impedance values of the samples decreased slightly, still maintaining values > 10^7 Ω.cm^2 for EP samples, about 10^8 Ω.cm^2 for EP/HDFS samples and EP/PVDF, > 10^8 Ω.cm^2 for samples EP/OTS and EP/PTFE. After 56 days of immersion in 3% NaCl, the $Z_{100\mathrm{mHz}}$ values of the samples are in the following order: EP/PTFE > EP/OTS > EP/HDFS = EP/PVDF > EP. The results show that modification of EP surface by organic silicon compounds (OTS and HDFS) and fluoropolymer layer increased the protective properties of EP coatings, and the treatment with PTFE and OTS provided a higher protection effect. It might be explained that OTS molecules and PTFE form a thicker layer than HDFS oligomers and can interact with EP hydroxyl groups. The surface analysis results also show that the EP/PTFE sample had a relatively uniform, tight surface and high contact angle. Hence, the water resistance is quite good, so the film and total resistance values at 100 mHz are higher than those of other samples. This result is consistent with other analytical results above.

Besides determining the film resistance value, $Z_{100\mathrm{mHz}}$, the CPE phase constant is also calculated. Variation of CPE values with exposure time to 3% NaCl solution of EP coating samples is presented in Figure 7. As the semicircle of the Nyquist impedance spectrum flattens, the phase constant CPE is used to replace the capacitance (C) in the equivalent electrical diagram and gives information about water absorption into the film, so it is characteristic of coating properties. At the beginning of immersion, the CPE values of the samples are not much different. When the immersion time increased, the CPE of the surface-modified EP samples did not change, while the EP samples increased after 56 days of immersion. When water penetrates the coating and causes it to swell, after a testing period, the coating is damaged, and CPE increases and n decreases. This phenomenon can be observed with the EP sample without surface modification. This result shows that treating the EP surface with organic silicon compounds and fluoropolymers prevents water from penetrating the coating.

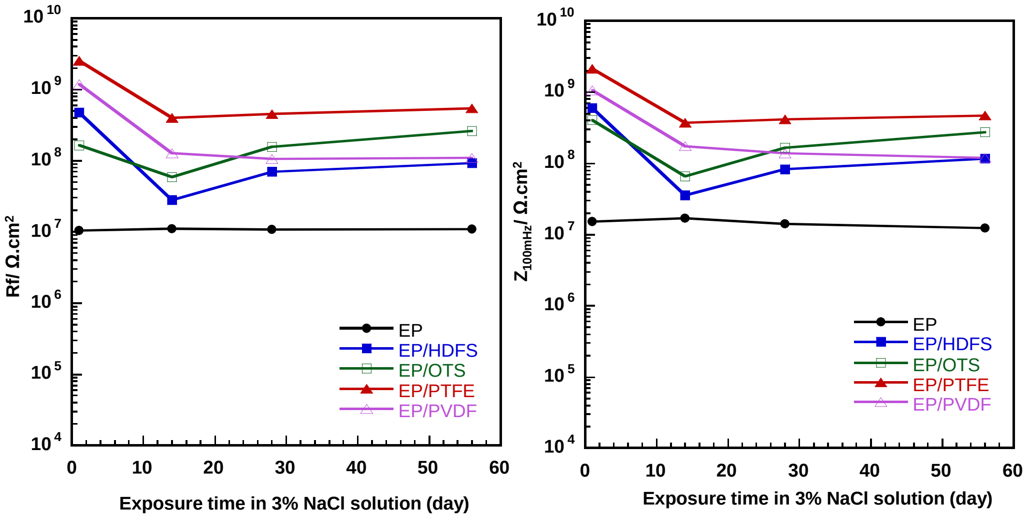


Figure 6. Variation of film resistance (R_f) values and Z_{100mHz} values with exposure time to 3 % NaCl solution of EP coating samples.

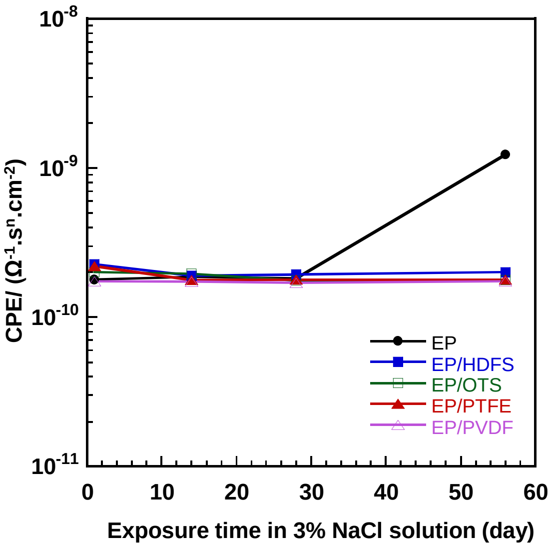


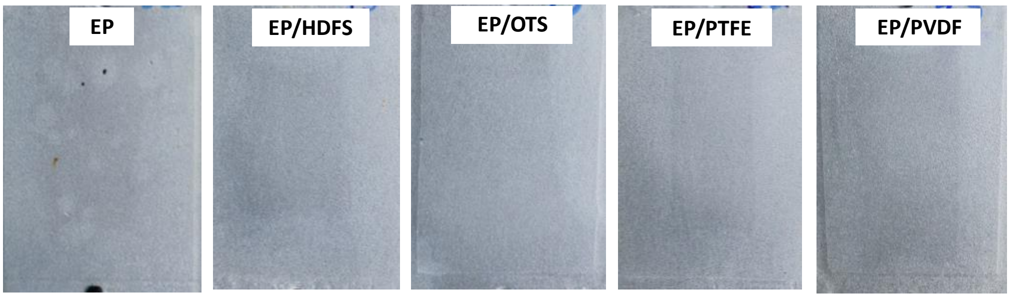
Figure 7. Variation of CPE values with exposure time to 3% NaCl solution of EP coating samples.

Thus, the electrochemical impedance results show that the presence of organic silicon compounds and fluoropolymers on the epoxy surface has increased the protective ability of the EP coating. This protection depends on the type of compound used and how the film is fabricated. Silicone compounds and fluoropolymers have almost the same protective effect. Among coatings, EP/OTS and EP/PTFE coatings have better protective effects than other coatings. EP/PTFE coating is made from the active gas phase, so the surface is tighter and uniform [13], so the protection ability is a little higher than EP/OTS coating. Besides, there are no hydrophilic groups in the molecule of PTFE, so the water resistance is higher than that of other compounds.

3.2.2. Salt spray test of coating systems

The salt spray test was used as an accelerated corrosion test to evaluate the corrosion resistance of the EP coating and EP coating modified with silicon compounds and fluoropolymer (EP/OTS coating, EP/HDFS coating, EP/PTFE coating, and EP/PVDF coating). The photographs of samples after 96 h and 336 h exposure to the salt spray test are shown in Figure 8. After 96 hours of testing, a few small rust spots and water infiltration spots appeared on the surface of the EP sample. This phenomenon was not observed for surface-modified EP samples with organosilicon compounds and fluoropolymers. After 336 hours of testing, the rust spot on the EP sample grew larger. Very small rust spots appear on the sample surface for EP/HDFS and EP/PVDF samples. For EP/OTS and EP/PTFE samples, rust spots on the sample's surface were not still observed. This result shows that treating EP surface with organic silicon compounds and fluoropolymers has increased corrosion resistance. When treating the surface of EP samples with OTS and PTFE compounds, the protective effect is higher than that of PVDF and HDFS compounds. This result is in agreement with the EIS measurement results.

After 96h



After 336h

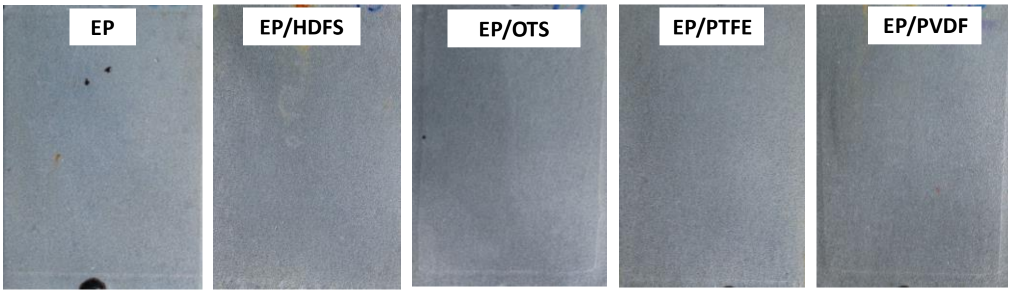


Figure 8. Photographs of coating samples after 96 h and 336 h exposure to salt spray test.

3.2.3. Wet adhesion test

The adhesion ability of the paint film was investigated using the grid adhesion measurement method according to ASTM D3359 standard, and classification results are presented in Table 3. It can be seen that the peeling area of surface-modified EP coatings with organic silicon compounds and fluoropolymers have lower values than that of the original EP layer. The peeling value of EP/HDFS and EP/PTFE coatings has the lowest value, about 24 %, followed by EP/OTS coatings at 34 % and EP/PVDF at 40 %. The good water resistance can explain this result (this is consistent with the high contact angle measurement results). When the epoxy coating surface is modified with organic silicon compounds and fluoropolymers, the electrolyte does not penetrate much into the coating, preventing the deterioration of the coating's shielding properties, thereby reducing the peeling of the epoxy coating.

Table 3. Classification of adhesion levels of tested paint systems according to ASTM D3359 standard, method B.

Sample	Removed area (%)	Classification
EP	86	0B
EP/HDFS	24	2B
EP/OTS	34	2B
EP/PFTE	24	2B
EP/PVDF	40	1B

3.2.4. Wear resistance of coatings

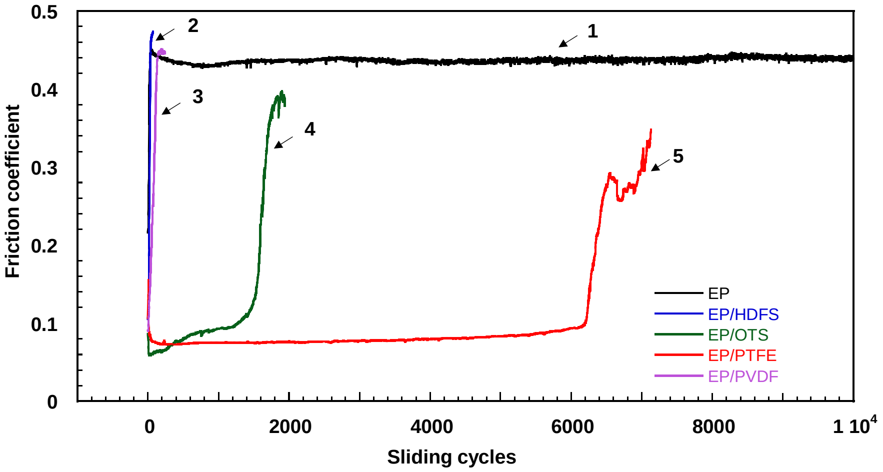


Figure 9. The friction coefficient as a function of number of sliding cycles: 1 – EP, 2 – EP/HDFS, 3 – EP/PVDF, 4 – EP/OTS, 5 – EP/PTFE.

The variations of the coefficient of friction against the sliding steel ball as a function of sliding cycles are shown in Figure 9. The EP, EP/HDFS and EP/PVDF coatings were destroyed after 30, 40, and 120 sliding cycles, respectively (Figure 9, curves 1, 2, 3). The EP/OTS sample showed more stable friction until 1950 sliding cycles with a coefficient friction value of about 0.4 (Figure 9, curve 4). The EP/PTFE coating remains in the contact area of surfaces up to 6350 sliding cycles with a coefficient friction value of about 0.2 (Figure 9, curve 5).

The increase in the wear resistance of EP after treating its surface with organosilicon compounds, especially OTS, is due to the lubricating effect of organosilicon compounds, which have several properties such as the mobility and flexibility of their main chain, weak inter molecular interactions, low surface tension and shear resistance and others [11, 18]. For the same reason, the coefficient of friction of the EP decreases after running-in of the friction pair from 0.22 to 0.08 when PTFE from the active gas phase is applied to its surface (Figure 9, curve 5). Polytetrafluoroethylene has the best antifriction and lubricating properties of the available structural and fluoroplastic materials studied in the work [19]. The fluorocarbon groups of PTFE also increase the hydrophobicity of EP. This result is in agreement with the previous result [13]. A more uniform PTFE layer on the surface of the EP compared to layers based on the PVDF compound.

4. CONCLUSIONS

The surface modification of the EP with organic silicon compounds and fluoropolymers increased its hydrophobicity, reduced the coefficient of friction, and improved anticorrosion behavior and wet adhesion. The maximum water contact angle is observed for EP/PTFE samples. In turn, using oligomethylsiloxane and polytetrafluoroethylene reduced the friction coefficient of the epoxy coating from 0.22 to 0.08 or 0.03. Moreover, the modification of the EP surface with PTFE from the active gas phase formed by electron beam dispersion significantly enhanced the corrosion protection performance of EP. The developed hydrophobic coating systems based on epoxy resin, organic silicon compounds, and fluoropolymers can be used to protect metal structures for various functional purposes from corrosion.

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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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