International Journal of Adhesion & Adhesives 63 (2015) 166–176

Contents lists available at ScienceDirect

International Journal of Adhesion & Adhesives

journal homepage: www.elsevier.com/locate/ijadhadh

Studying various mixtures of 3-aminopropyltriethoxysilane (APS) and tetraethylorthosilicate (TEOS) silanes on the corrosion resistance of mild steel and adhesion properties of epoxy coating

B. Ramezanzadeh [*], E. Raeisi, M. Mahdavian

Department of Surface Coatings and Corrosion, Institute for Color Science and Technology (ICST), PO 16765-654, Tehran, Iran

ARTICLE INFO

Article history:
Accepted 8 September 2015
Available online 16 September 2015

Keywords:
Silane
Epoxy coating
Contact angle
EIS
FE-SEM
EDS
Pull-off adhesion

ABSTRACT

Different mixtures of tetraethylorthosilicate (TEOS) and 3-aminopropyltriethoxysilane (APS), i.e. 100/0, 70/30, 50/50, 30/70 and 0/100, were applied on mild steel samples. The morphology and composition of the silane coatings were investigated by field emission scanning electron microscopy (FE-SEM), energy dispersive spectroscopy (EDS) and contact angle analysis. Open circuit potential (OCP) and electrochemical impedance measurements were performed on the bare steel and silane coated samples by electrochemical impedance spectroscopy (EIS). Results showed that a mixture of 70/30 of TEOS/APS resulted in a more consecutive and compact film formation on the steel surface. It was shown that the mixture of TEOS/APS provided better corrosion protection properties than the single ones. The film composed of APS decreased the contact angle more than TEOS. An epoxy coating was applied on the surface of steel samples treated by various mixtures of silanes. Pull-off and salt spray tests were performed on these samples to investigate the effects of surface treatment on the adhesion and corrosion protection properties of the epoxy coating. It was found that the mixture of silanes significantly enhanced the adhesion and corrosion protection properties of the epoxy coating.

1. Introduction

Iron and its alloys have been widely used in industries because of their stiffness and high strength to weight characteristics. However, they are highly susceptible to corrosion in aggressive environments. Many different methods have been utilized in order to protect steel structures against corrosion. Among them, conversion coatings [1–4], corrosion inhibitors [5–8] and organic paints [9–11] have been widely used to increase the corrosion resistance of metal substrates. Organic coatings can protect metals from corrosion through the production of a barrier between the metal surface and the corrosive environment. However, most of the organic coatings are osmotic to corrosive species such as oxygen, water and ions. This is responsible for the decrease of coating adhesion, and thus accelerating the corrosion of the metal beneath the coating. Also, the cathodic reaction ($2H_2O+O_2+4e \rightarrow 4OH^-$) occurs at cathodic regions leading to an increase in pH at the coating/metal interface. The adhesion bonds are damaged and coating delamination from the metal surface occurs at alkaline pHs. This results in a decrease of the coating corrosion protection performance [12,13].

Attempts have been carried out to improve the adhesion properties of organic coatings on metal surfaces. The presence of different kinds of contaminants, i.e. oil, dust, metal oxide/hydroxide and salts, on the metal surface is responsible for poor organic coating adhesion. Removing such contaminations by physical and/or chemical pretreatment methods can provide good adhesion between the organic coating and metal substrate. It has been shown that the chemical treatment of metals is an effective method to obtain excellent adhesion and corrosion protection properties for organic coatings. The most popular chemical treatment methods are conversion coatings and silane based treatments through sol–gel processes. Chemical treatments, i.e. zinc phosphate [4], cerium [14] and zirconium [15] based conversion coatings, of metals have been considered as a useful method to increase the corrosion resistance of steel. Also, this method of surface treatment can promote the adhesion of paint, varnish and lacquer on the steel substrate. It has also been shown that phosphate based conversion coatings can provide some protection against under-paint corrosion [16–18]. However, phosphate coatings are porous and contains some micro cracks that cannot provide promising corrosion resistance for the steel substrate. Chromates have been used as sealing agents for the phosphate layers to

---

[*] Corresponding author. Tel.: +98 2122969771; fax: +98 2122947537.
E-mail addresses: ramezanzadeh@aut.ac.ir, ramezanzadeh-bh@icrc.ac.ir (B. Ramezanzadeh).

http://dx.doi.org/10.1016/j.ijadhadh.2015.09.007
0143-7496/© 2015 Elsevier Ltd. All rights reserved.

enhance its corrosion resistance [19]. Therefore, dipping phosphated samples in a chemical bath containing hexavalent chromium has been a common and promising method to obtain a surface with less porosity and higher corrosion resistance. However, due to the toxic and carcinogenic nature of chromate based conversion coatings, the use of these coatings has been extremely restricted in recent decades. Considerable efforts have been directed towards developing alternative and environmentally acceptable chrome-free pretreatment for metals. This has resulted in the use of silane pre-treatments. Silanes have been introduced as adhesion promoters which can provide superior protection for the metal surface. The silane based coatings can be applied on the metal surface in a process named sol–gel. It can be described as the creation of an oxide network by progressive condensation reactions of molecular precursors in a liquid medium [20-22]. Recently, researchers attentions have been directed at developing sol–gel based silane coatings with enhanced adhesion and corrosion protection properties. These have been based on modifications of the bulk properties of the silane coatings by addition of nanoparticles and/or corrosion inhibitors [23-28] and developing mixture of silanes.

It has been shown that surface treatment of metals by a combination of two silanes can give good corrosion protection performance. Lei et al. [29] investigated the effect of a mixture of γ-amino propyltriethoxysilane and γ-glycidoxypropyltrimethoxysilane on the corrosion resistance of galvanized steel. They found that such a combination can provide better corrosion inhibition than a coating which was composed of the silane alone. Deflorian et al. [30] studied the corrosion protection performance of mixtures of three different silanes such as those based upon γ-glycidoxypropiltrimethoxysilane (γ-GPS), tetraethoxysilane (TEOS) and methyltriethoxysilane (MTES) on the steel substrate. They showed that the mixture of silanes could provide better corrosion protection properties than each silane used alone.

This study aims at surface treatment of steel by a series of silane based coatings obtained through mixing tetraethylorthosilicate (TEOS, $C_8H_{20}O_4Si$) and (3-Aminopropyl) triethoxysilane (APS,$C_9H_{23}NO_3Si$). FE-SEM, EDS and contact angle analysis were utilized to characterize the surface morphology and composition of the silane coatings. Also, OCP and EIS measurements were performed to investigate the corrosion resistance of the coatings. Epoxy coating was applied on the silane treated samples. The adhesion properties and corrosion protection properties of the epoxy coating were studied by pull-off and salt spray tests, respectively.

2. Experimental

2.1. Materials

St-37 panels (150 mm × 100 mm × 2 mm) were purchased from Foolad Mobarakeh Co (Iran). The composition of the steel is given in Table 1.

Table 1 Phosphoric acid (85%) and benzotriazole ($C_6H_5N_3$) (BTH) were provided by Merck Co. to prepare acid washing solutions. Silane solutions were prepared using tetraethylorthosilicate (TEOS, $C_8H_{20}O_4Si$) and (3-Aminopropyl)triethoxysilane (APS, $C_9H_{23}NO_3Si$). The chemical structures of the silanes are shown in Fig. 1.

Table 1
Chemical composition of St-37 type steel substrate.

Elements	Fe	C	Si	Mn	P	S	Al
Composition (wt%)	99.03	0.18	0.33	0.32	0.05	0.05	0.04

TEOS and APS were purchased from Aldrich Co. (Germany) and used without further purification. Ethanol (C_2H_5OH, 98%) and acetic acid ($C_2H_4O_2$) were purchased from Merck Co. Sodium hydroxide (NaOH) was purchased from Merck Co. as a pH modifier.

Araldite GZ7 7071 × 75 was provided from Huntsman Co. and used as epoxy resin. The solid content, epoxy value and density of the epoxy resin were 74–76%, 0.1492–0.1666 Eq/100 g, and 1.08 g cm^{-3}, respectively. An amido polyamide, CRAYAMID 115, was purchased from Arkema Co. and used as the epoxy hardener. The solid content, density and viscosity at 40 °C of the hardener were 50%, 0.97 g/cm^3 and 50,000 cps, respectively.

2.2. Silane preparation

A series of silane solutions were prepared using 5 mixtures of TEOS and APS in deionized water. The composition of each solution is given in Table 2. Using acetic acid the pH of all silane solutions was adjusted at 4.5. First, the appropriate amounts of TEOS and APS were mixed and then the mixtures were stirred for 3 h to provide the hydrolysis condition. The mixtures of the silanes were clear after 3 h indicating the hydrolysis of silanes and low degree of condensation at acidic pH.

2.3. Surface preparation and application

The steel panels were cleaned before silane treatment. For this purpose, samples were abraded by emery papers of 600, 800 and 1200 grades followed by acetone degreasing. Then, they were treated by acid phosphoric washing solution. This was done to remove any oxide/hydroxide layers remaining on the steel surface. The acid washing solution was prepared using 22.58 cm^3 (0.33 M) of phosphoric acid (98%) and 0.115 cm^3 (1 mM) of BTH in 1000 cm^3 deionized water. BTH was used as a corrosion inhibitor to prevent the steel samples from corrosion after the washing process. The acid phosphoric solution was then sprayed on the pre-cleaned steel panels for 10 s. Samples were then washed with deionized water and dried with warm air at 40 °C. The acid washing process was done in order to ensure the complete removal of the oxide/hydroxide layer

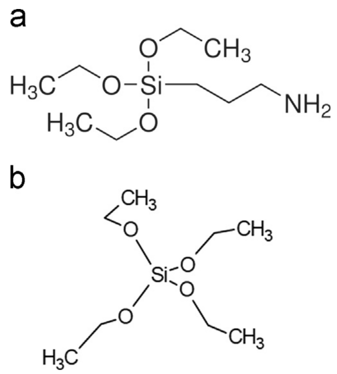

Fig. 1. Chemical structures of (a) APS and (b) TEOS.

Table 2
The composition of silane solutions prepared based on various mixtures of TEOS/APS.

Element (%)	Water (g)	Ethanol (g)	TEOS (g)	APS (g)
T/A: 100/0	1.62	93.38	5.0	0.0
T/A: 70/30	1.48	93.52	3.44	1.56
T/A: 50/50	1.38	93.62	2.43	2.57
T/A: 30/70	1.29	93.71	1.45	3.55
T/A: 0/100	1.15	93.84	0.0	5.0

from the steel surface. Also, the phosphoric acid solution could produce a thin iron phosphate layer on the steel surface helping the silane layer film deposition on the steel surface.

Finally, the cleaned steel panels were coated with different silane mixtures. For this purpose, the steel panels were immersed in the silane solutions for 1 min followed by drying in warm air (40 °C). This procedure was repeated three times to ensure that a thick silane layer was formed on the samples. Samples were then washed with deionized water and dried. The silane coated samples were cured at 120 °C for 1 h.

2.4. Epoxy coating preparation and application

Additives, i.e. leveling agent (BYK-306: 0.5 wt%), defoamer (Efka-2025: 0.1 wt%) and dispersing agent (Delta-4242: 1 wt% of total weight of pigments and fillers), pigments and fillers, i.e. red iron oxide (10 wt%), TiO_2 (14 wt%) and talc mineral (20 wt%), solvents, i.e. toluene (10 wt%), were added to the epoxy resin. It was mixed for 3 h under high shear mixer to provide dispersion of the pigments and fillers (the average particle size < 15 μm). Then, the polyamide curing agent was added to the mixture at a weight ratio of 12:3 (polyamide: epoxy) and mixed for 10 min. The prepared coating was applied on the bare steel and on the silane coated samples by an air spray. Samples were then maintained at room temperature for 15 days to ensure the full cure. The dry thickness of the coating was 70 ± 5 μm.

2.5. Techniques

2.5.1. Surface analysis

The surface morphology of the steel samples modified with various silane mixtures was studied by FE-SEM (Mira) equipped with EDS model SAMx. Static contact angles were measured on different samples by an OCA 15 plus type contact angle measuring system using distilled water as probe liquid at a temperature and humidity of 25 ± 2 °C and 30 ± 5%, respectively. In this regard, a small drop of distilled water (2–3 µl) was applied on the surface of the samples. The shape of droplet was recorded by a Canon type digital camera after 10 s. The images were transmitted to a personal computer for evaluation. Using an image analysis system (G2/G40), the contact angle values were calculated.

2.5.2. Electrochemical measurements

The open circuit potential (OCP) of the steel samples (1 cm^2) modified with different mixtures of silanes was measured in 3.5 wt% NaCl solution with respect to an Ag/AgCl reference electrode. The corrosion resistance of the samples with and without silane treatment was investigated by electrochemical impedance spectroscopy. The EIS analysis was done in a conventional three-electrode cell including saturated Ag/AgCl as the reference electrode, platinum as the counter electrode and the coated steel specimen as the working electrode. The measurements were done in the frequency range of 10 kHz to10 mHz (peak to zero) and at 10 mV amplitude sinusoidal voltage by using the Ivium Compactstat electrochemical work station at open circuit potential. EIS analysis was carried out on 1 cm^2 of the coated samples immersed in 3.5 wt% NaCl solution at different immersion times. Also, the measurements were implemented 3 times to ensure the repeatability of the measurements.

2.5.3. Salt spray test

Salt spray test was performed on the steel samples (with and without silane treatment) coated with epoxy coating. The salt spray test was performed according to ASTM B117 for 300 h.

2.5.4. Pull-off adhesion test

The adhesion strength values of the epoxy coatings applied on the samples treated with various silane mixtures were obtained by a Posi test-pull-off adhesion tester (DEFELSKO). For this purpose the aluminum dollies were glued on the surface of the epoxy coating using a two-part Araldite 2015 (Huntsman Advanced Materials, Germany) adhesive. Samples were then kept at ambient temperature for 24 h to ensure that the glue was cured completely. Finally, a slot was made around the dollies and they were pulled at a speed of 10 mm/min normal to the coating surface until the epoxy coating was detached from the steel substrate. All tests were carried out on three samples and the average value was considered.

3. Results and discussion

3.1. Samples without organic coating

3.1.1. Surface analysis

Fig. 2 shows the FE-SEM images of the bare steel and those treated by various mixtures of silanes. The surface morphology of the samples coated with various mixtures (w/w) of TEOS/APS, i.e. 100/0, 70/30, 50/50, 30/70, 0/100, was studied by FE-SEM.

Fig. 2 shows that the bare steel surface is rough with a considerable number of grooves and ripple created during the surface preparation process by sand paper. However, the morphology of the steel substrates was considerably changed after treatment by silane coating. A layer of silane covered the whole steel surface and the surface features, i.e. grooves had disappeared. It can be obviously seen from this figure that as the ratio of TEOS/APS decreased, i.e. T/A: 70/30 and T/A: 50/50, a more compact and homogenous silane layer formed on the steel surface. It can be seen that the surface morphology of the sample coated with T/A: 70/30 differs from others. Replacing 30% of TEOS by APS in the silane mixture resulted in the most appropriate surface morphology of the silane coating. There were no discontinuities and cracks on this sample. However, further decreasing of the TEOS/APS ratio, i.e. T/A: 30/70 and T/A: 0/100, resulted in thin silane layer formation on the steel surface. In fact, APS has only three functionalities that could participate in the film formation process during the condensation stage. Because of this, the APS cannot form thick film. However, TEOS has four functionalities that can form a better network and help the APS to form a thicker film. Grooves and ripples were seen on the surface of the sample treated only with APS. This confirms that the APS cannot form proper film on the steel compared to TEOS. Furthermore, it can be said that the mixture of 70/30 of TEOS/APS resulted in the best surface morphology from the point of crack free and more compact film formation. It can be seen in Fig. 3 that the thickness of the film formed on this sample is 200 ± 50 nm. However, the film thickness cannot be determined on other samples in this way indicating their very low thickness (below 100 nm).

The EDS analysis was performed to characterize the surface composition of the samples. The EDS spectra and mapping results are presented in Figs. 4 and 5. Also, the results derived from these figures are given in Table 3.

From Table 3 it can be seen that N, O, Fe, Si and C are the elements which were detected on the steel surface treated by silane coatings. According to Table 3 it can be seen that the amount of Fe significantly decreased and O content increased after silanization. Detection of Si and C on the silane coated samples indicates that a thin silane film was formed on the surface of the sample. Recognition of N and C elements on the sample treated with only TEOS can be attributed to the adsorption of benzotriazole molecules on the steel surface during the acid washing process. As the ratio of T/A decreased the amount of Si, C and N increased. These elements correspond to the Si–O–Si or

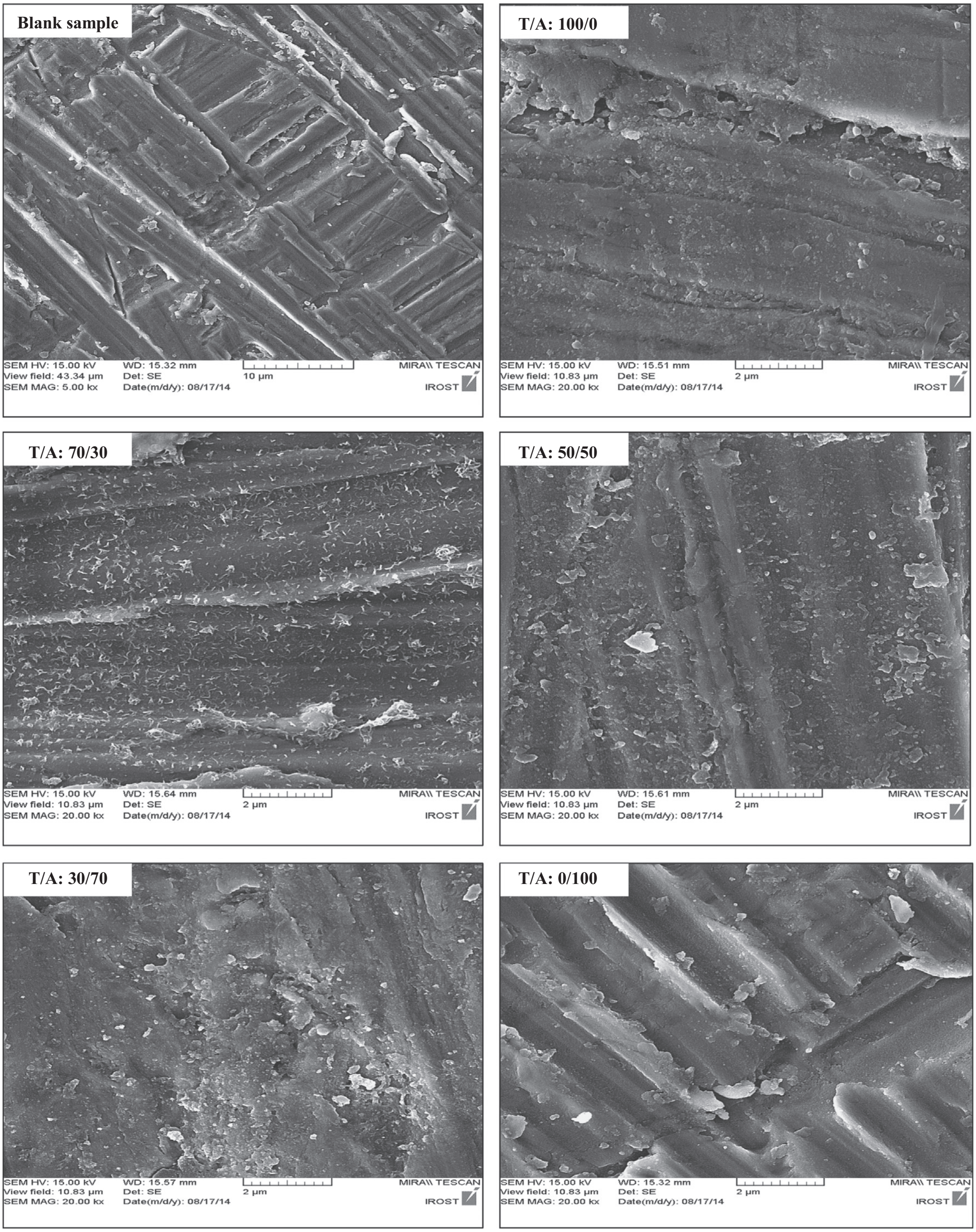

Fig. 2. FE-SEM micrographs obtained from the surface of steel panels treated with various mixtures of silanes.

O–Si–O, Si–C and NH_2 groups in the silane films. The highest amount of C and Si was seen on the sample treated by T/A: 70/30. Further replacement of TEOS with APS in the mixture of silane resulted in the decrease of Si and C. These observations confirm that the film formed on the steel surface in the silane solution of T/A: 70/30 is thicker than other samples. All of these observations demonstrate that the partial replacement of the TEOS with APS resulted in better silane film formation on the steel surface.

The surface chemistry of the bare steel and those coated with mixtures of silanes was evaluated by contact angle measurements. The water contact angle values were measured on different samples and the results are presented in Fig. 6.

The work of adhesion (W_A) and surface free energy (γ_{sv}) values were calculated for different samples through Young's (Eq.(1)) and Neumann [31] (Eq. (2)) equations, respectively.

$$W_A = \gamma_{lv}(1 + \cos\theta) \tag{1}$$

$$W_A = 2(\gamma_{lv}\gamma_{sv})^{1/2}\exp\left[-\beta(\gamma_{lv}-\gamma_{sv})^2\right] \tag{2}$$

where γ_{lv} and γ_{sv} are the surface tension of water (γ_{lv}=72.8 mJ/m^2) and surface free energy of the film, respectively. θ is water contact angle and the value of β is equated to 0.000125 ± 0.000010 (mJ/m^2)$^{-2}$. To calculate surface free energy, the work of adhesion (W_A) was first calculated according to Eq. (1) (Young equation).

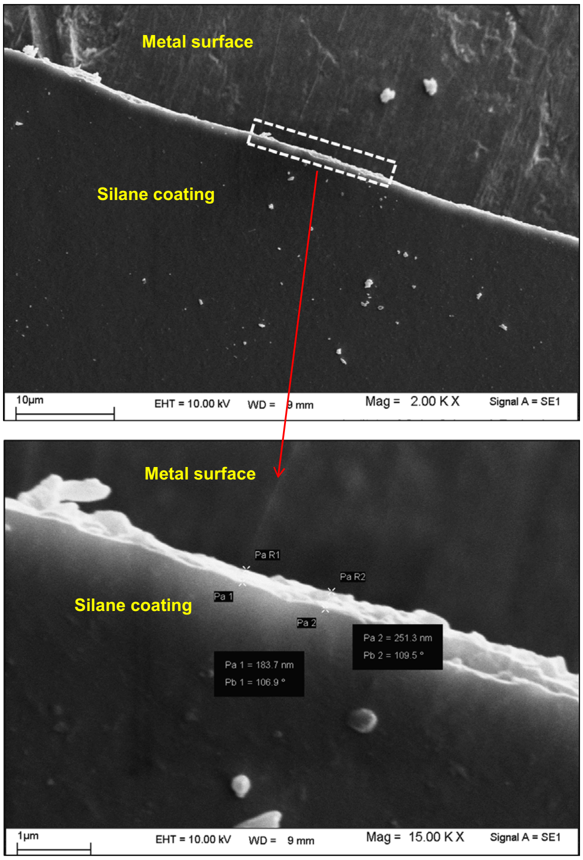

Fig. 3. FE-SEM micrographs at two magnification obtained from the cross-section of the mixture of 70/30 of T/A on the steel surface.

The surface free energy (γ_{sv}) was then calculated by Eq. (2). The values of W_A and γ_{sv} for the samples treated by various silane mixtures are presented in Table 4.

It can be seen from Fig. 6 that the contact angle of the bare steel is 98.7°. Results show that silanization of the steel surface by TEOS decreased the contact angle up to 89° and increased W_A and γ_{sv} values. The contact angle was significantly decreased and the W_A and γ_{sv} were noticeably increased as the ratio of TEOS/APS decreased. The lowest contact angle and the highest W_A and γ_{sv} values were seen on the sample treated with only APS. This observation indicates that the APS film provided a more hydrophilic surface than TEOS film. In fact, the end –NH_2 group in the chemical structure of the APS may be responsible for the hydrophilicity of the steel surface. The hydrogen bonds between the –NH_2 groups and water molecules are responsible for the better water molecule spreading on the steel surface causing the decrease of contact angle. The TEOS condensation on the steel surface results in the formation of film composed of –Si–O–Si– cross-links. The –Si–O–Si– cross-links provide less hydrophilicity than –NH_2 groups. Because of this, the film consisting of APS showed higher surface free energy and therefore hydrophilicity than TEOS. This means that acid washing of steel prior to silane treatment increased surface hydrophobicity. It seems that the organic BTH molecules adsorption on the steel surface during the acid washing resulted in lower steel surface hydrophilicity than silane treated samples.

3.1.2. Electrochemical properties

3.1.2.1. OCP measurements. The steel samples treated by various silane mixtures were immersed in the 3.5 wt% NaCl solution and their OCP values were measured at different times with respect to Ag/AgCl reference electrode. The results are given in Fig. 7.

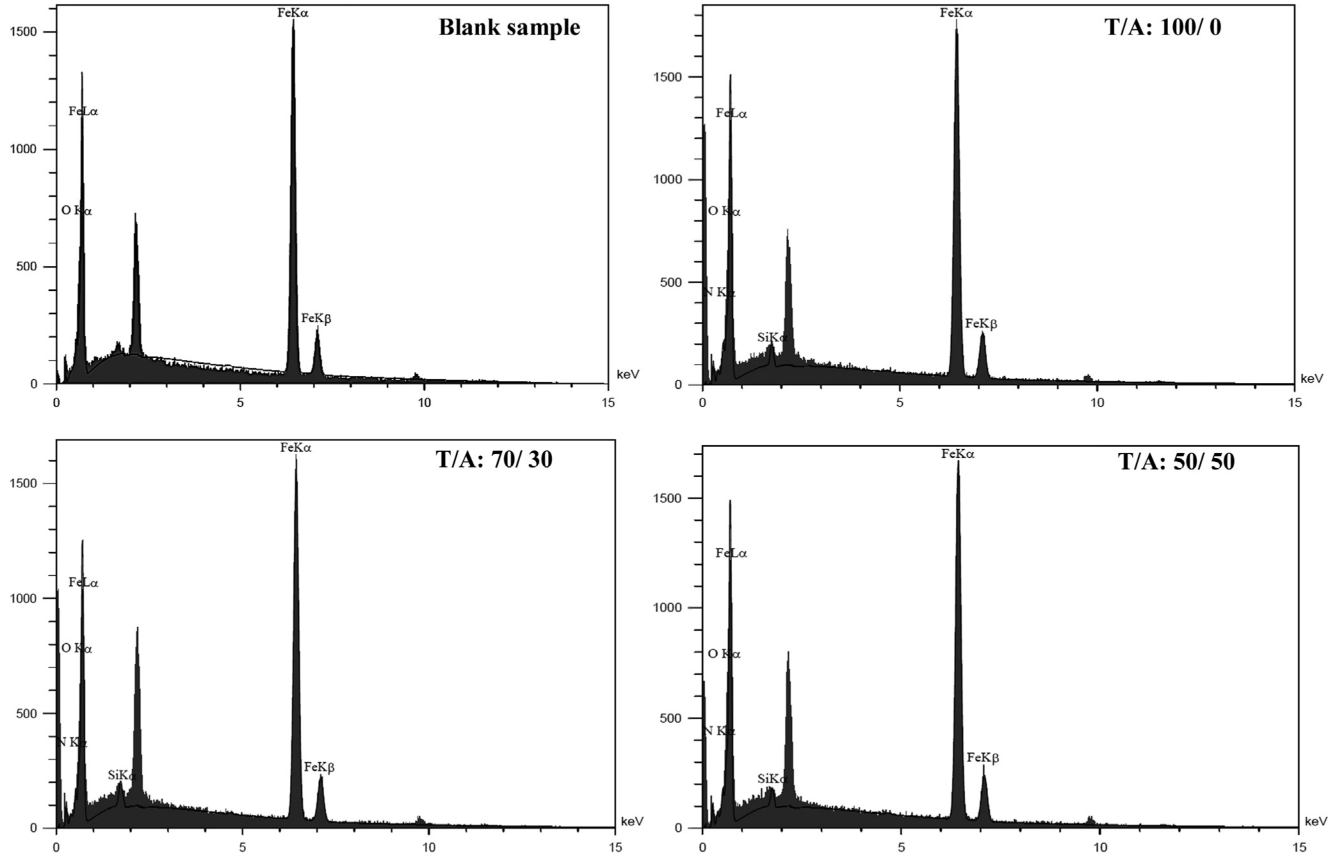

Fig. 4. EDS analysis from the surface of steel samples coated by the mixtures of silanes.

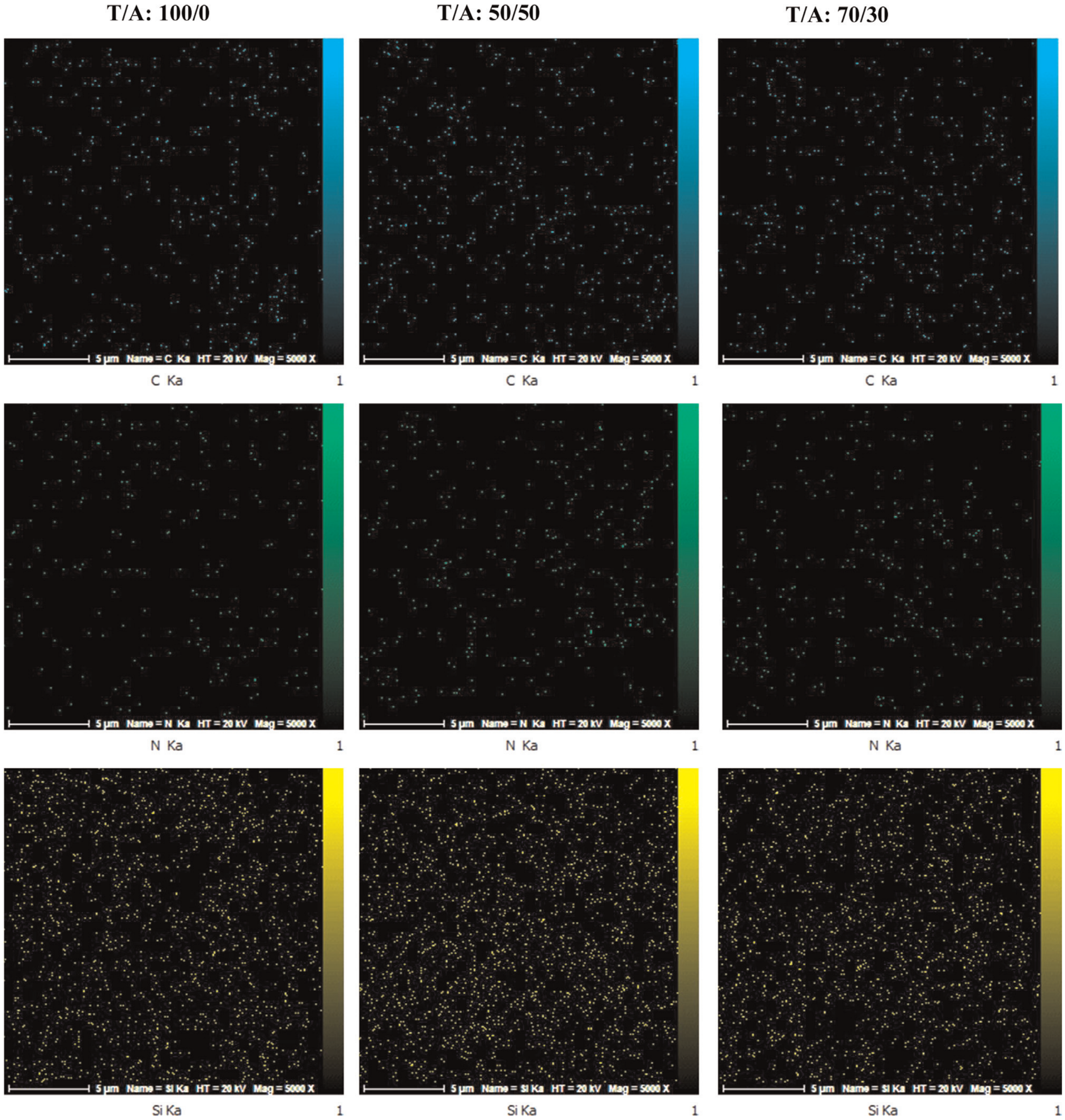

Fig. 5. EDS map analysis from the surface of steel samples coated by the mixtures of silanes.

Table 3
Elemental composition (obtained from EDS analysis) of the surface of steel samples modified with various silane composite coatings.

Element (%)	N	O	Fe	Si	C
Blank sample	–	2.2	97.80	–	–
T/A: 100/0	6.5	7.90	71.0	1.30	12.8
T/A: 70/30	5.0	4.8	73.80	1.9	14.5
T/A: 50/50	4.2	7.4	72.60	1.7	14.0
T/A: 30/70	5.0	6.8	73.10	1.5	13.60
T/A: 0/100	5.8	6.5	73.30	1.2	13.30

From Fig. 7 it can be seen that the OCP of the steel sample decreased as the immersion time increased. The same trend was seen for the steel samples coated with various mixtures of silanes. However, the decrease in OCP with the bare steel was most significant at the initial stage of the immersion (first 20 min). The decrease in OCP of all samples continued up to 40 min and then the OCP reached a constant

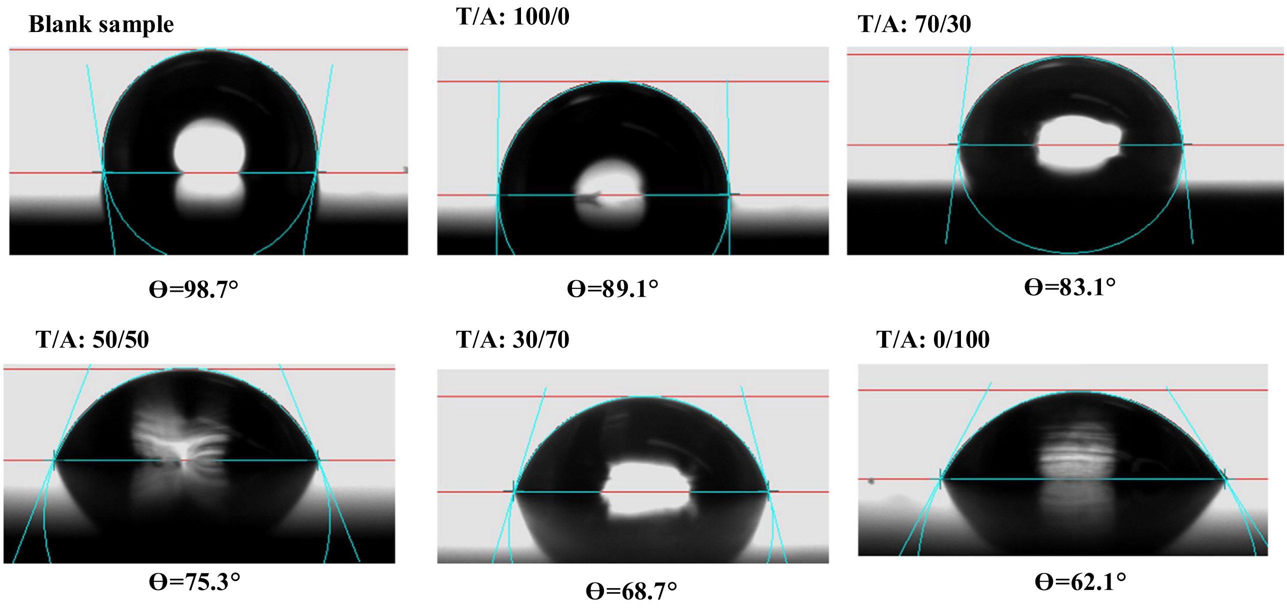

Fig. 6. Contact angle measurements of using water droplet on the surface of steel samples coated by the mixtures of silanes.

Table 4
The values of work of adhesion (W_A) and surface free energy (γ_{sv}) of the samples treated with various mixtures of TEOS/APS.

Parameter	W_A (mJ)	γ_{sv} (mJ/m^2)
Blank sample	61.8 ± 2.0	23.3 ± 1.8
T/A: 100/0	73.9 ± 3.0	29.3 ± 2.0
T/A: 70/30	81.5 ± 2.0	33.0 ± 1.0
T/A: 50/50	91.2 ± 4.0	38.0 ± 2.0
T/A: 30/70	99.2 ± 3.0	42.4 ± 2.0
T/A: 0/100	106.8 ± 1.0	46.0 ± 2.0

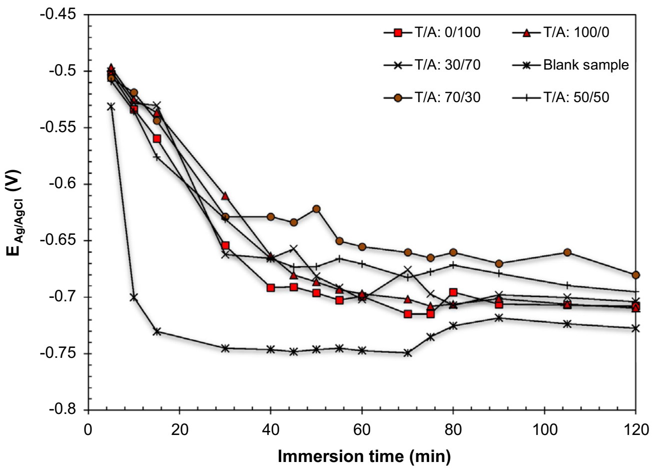

Fig. 7. Variation of OCP vs. Ag/AgCl as a function of immersion time for the steel samples treated with various silane mixtures.

value with slight variation with further increasing of the immersion time. The decrease in OCP with increasing immersion time can be attributed to the corrosive electrolyte diffusion into the silane coating/metal interface. It can be seen from the OCP results that all silane coated samples had OCP values greater (more positive) than bare steel. This confirms that the silane coatings could form a barrier layer on the steel surface restricting the corrosion species, i.e. Cl^-, H_2O and O_2, access to the active sites of the steel surface. It can be seen that the samples coated with the mixture of silanes showed higher OCP values than those treated with only TEOS or APS. Among different samples, the one treated with T/A:70/30 showed the most positive OCP values even after 120 min immersion. This finding may indicate that this coating had higher barrier characteristics than those treated only with TEOS or APS. In fact, the more compact film with greater thickness formed on the sample treated by the mixture of T/A:70/30 is responsible for the greater barrier properties of this film. For further characterization of the effect of mixture of silanes on the electrochemical action of the steel, the EIS measurements were carried out on different samples at different immersion times.

3.1.2.2. EIS measurements. The EIS analysis was performed to calculate the corrosion resistance of the bare steel and silane coated samples at different immersion times in 3.5 wt% NaCl solution. The Bode diagrams of different samples are presented in Fig. 8. Also, the impedance values were obtained at low frequency (10 mHz) from the Bode diagrams and the results are presented in Fig. 9.

From Fig. 9 it can be seen that the impedance value of the bare steel sample is much lower than those treated with mixture of silanes. At the beginning of immersion (15 min) the sample treated with TEOS showed higher corrosion resistance than the one treated with APS. It can be seen that the mixture of T/A, i.e. 70/30 and 50/50, showed higher impedance values than other samples. This observation confirms the OCP results that the mixture of silanes especially T/A:70/30, enhanced the steel resistance against

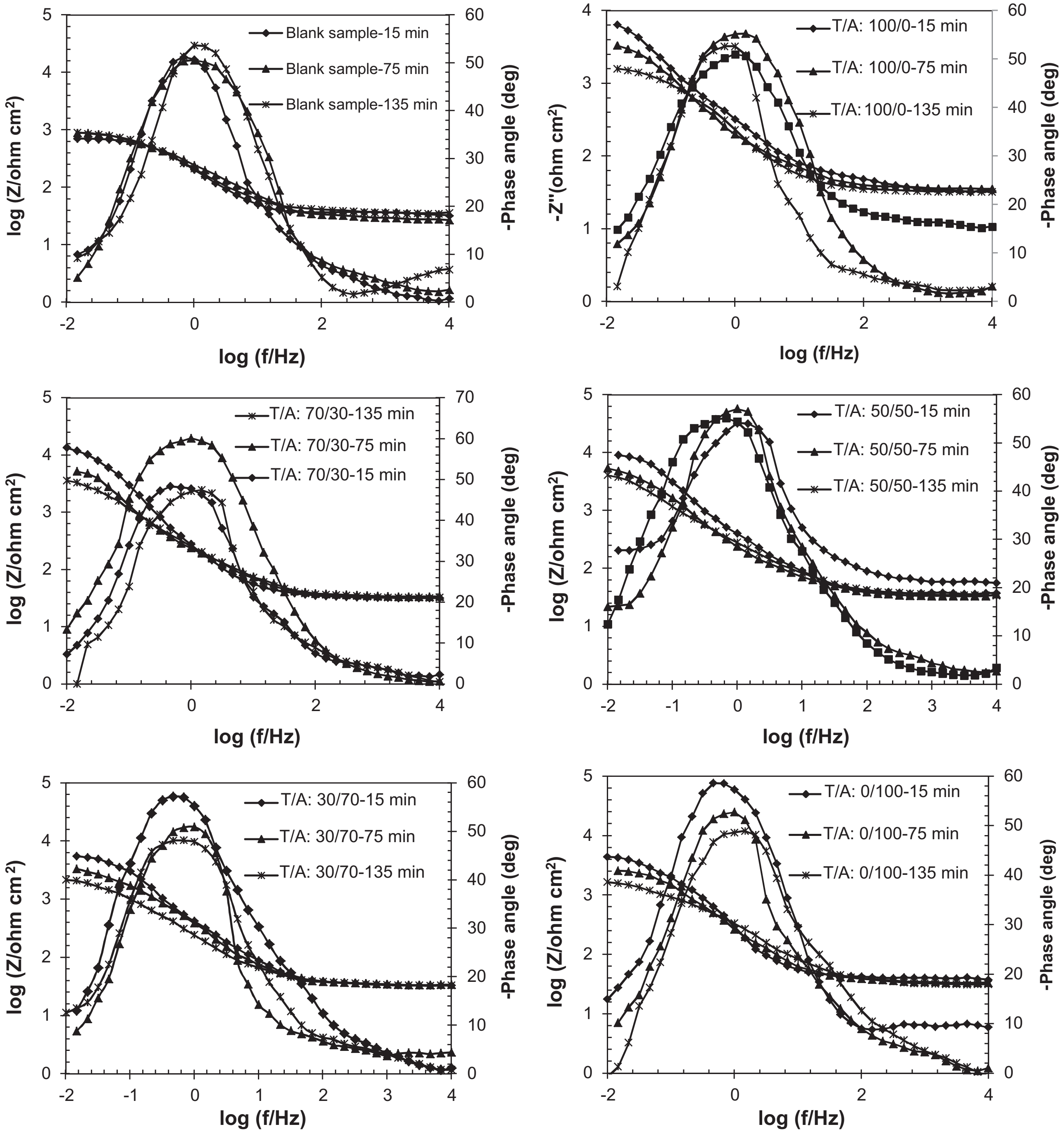

Fig. 8. Bode diagrams obtained from EIS analysis for the steel samples coated with various silane mixtures immersed in 3.5 wt% NaCl solution for 15, 75 and 135 min.

corrosion more than other samples. The silane coatings formed from the solutions containing mixtures of 70/30 and 50/50 of T/A resulted in the best corrosion protection properties on the steel surface. It can be seen that the impedance decreased for all samples as the immersion time increased. This behavior may be attributed to electrolyte diffusion into the coating causing the coating degradation and the decrease of coating barrier characteristic. The higher impedance value of the mixture of silanes may imply such silane combinations provided more corrosion protective films. The denser film with greater thickness of the mixture of silanes may be responsible for its greater barrier performance. It can be seen that APS alone cannot provide a good corrosion resistant film on the steel surface due to its lower film formation properties than TEOS. However, APS could enhance the film formation properties of the TEOS.

3.2. Samples with organic coating

3.2.1. Pull-off adhesion test

The epoxy coating was applied on the steel substrates modified with various mixtures of silanes. The adhesion of the samples was determined by pull-off test. The values of adhesion and the type of failure for the samples are presented in Fig. 10.

From Fig. 10 it can be seen that the surface treatment of steel caused an increase in pull-off strength of the epoxy coating over the steel substrate. Adhesive failure was seen on the bare steel

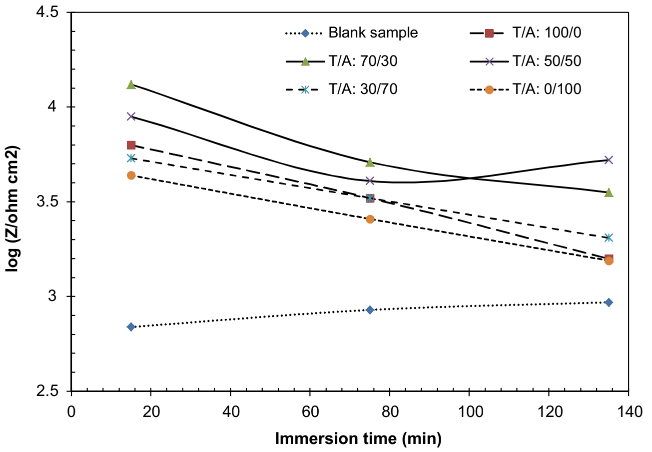

Fig. 9. Variation of impedance at 10 mHz versus immersion time for the steel samples coated with various silane mixtures immersed in 3.5 wt% NaCl solution.

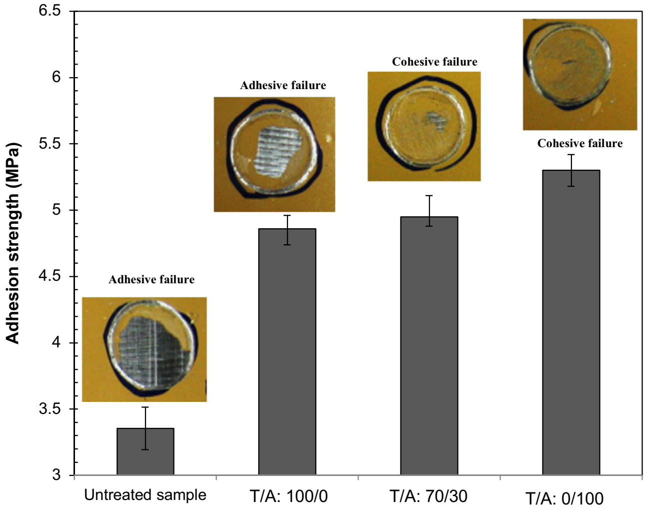

Fig. 10. Pull-off test performed on the steel samples (without and with silane treatment) coated with epoxy coating.

indicating poor adhesion of the epoxy coating on this sample. It can be seen from the results that T/A:70/30 and T/A:0/100 samples enhanced the adhesion of the epoxy coating to the steel surface greater than T/A:100/0. Also, cohesive failure was seen on the samples treated by T/A:70/30 and T/A:0/100. This indicates that the presence of APS in the silane mixture could significantly enhance the adhesion properties of the epoxy coating on the steel surface. This can be attributed to two main reasons. First, the presence of APS in the mixture of silanes caused a significant decrease of contact angle and increase of wetting properties of the steel surface. This caused the adhesion properties enhancement of the epoxy coating. The second reason for the enhanced adhesion properties is the effect of APS on the chemical reaction between the epoxy coating and silane coating. The epoxy coating can produce chemical bonds with the steel surface through epoxide ring reactions with NH_2 groups of the silane coating [32,33].

3.2.2. Salt spray test

The effects of silane treatment of the steel substrate on the corrosion protection properties of the epoxy coating were studied by salt spray test. The results are given in Fig. 11.

It can be seen from Fig. 11 that some blisters appeared at scribes on the sample without silane treatment. Also, coating delamination at scribes was observed for this sample. The hydroxyl ions creation at the cathodic regions ($2H_2O+O_2+4e \rightarrow 4OH^-$) is responsible for the adhesion bond damage and coating disbondment from the steel surface. However, no blisters were seen around scribes of the sample modified with a mixture of T/A:70/30 silanes. The silane coating could enhance the corrosion protection properties of the epoxy coating on the steel surface through increasing the adhesion of the epoxy coating and corrosion resistance of the steel substrate.

4. Conclusions

Silane coatings based on mixtures of TEOS/APS were applied on the steel surface. The surface morphology of the silane treated samples was studied by FE-SEM and EDS analyzes. It was shown that mixtures of silanes, i.e. T/A:70/30 and T/A:50/50, resulted in the formation of more compact films on the steel surface compared to the film composed of the APS and TEOS alone. APS and TEOS formed cross-linked films on the steel surface. The increase of APS content in the mixture of silanes caused a significant decrease of the contact angle and increase of surface hydrophilicity. Also, the silane coating composed of

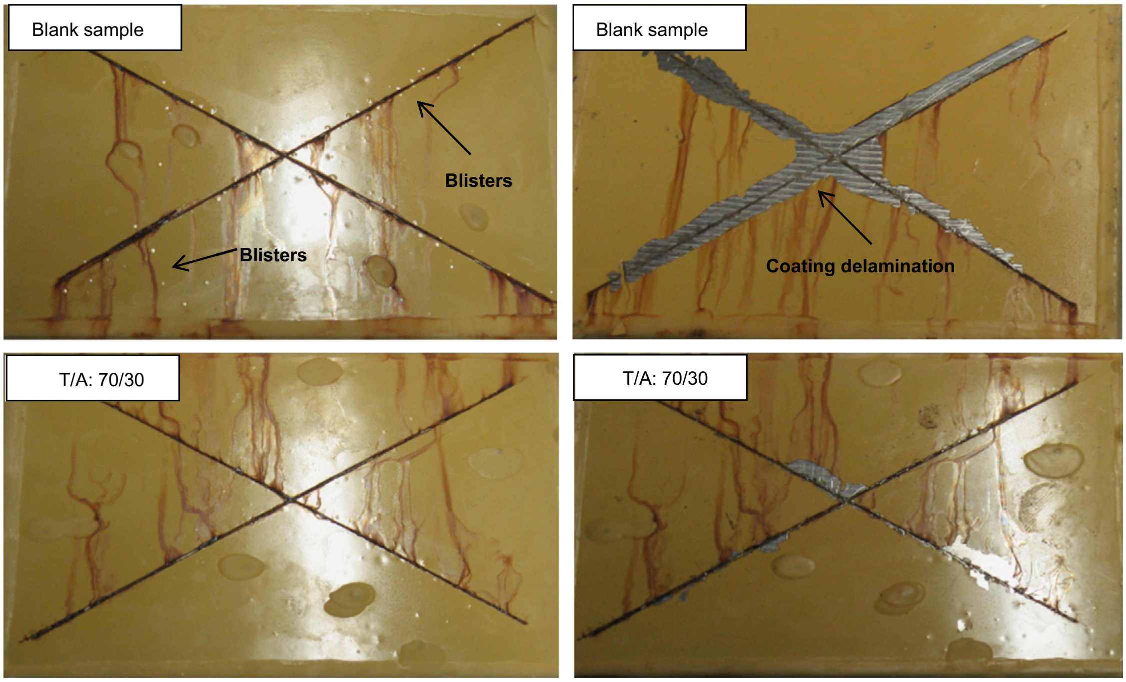

Fig. 11. Salt spray test performed on the steel samples (without and with silane treatment) coated with epoxy coating for 300 h.

the mixture of 70/30 of TEOS/APS can provide a better corrosion inhibition performance than the coating composed of the silanes alone. The mixture of silanes enhanced the adhesion and corrosion protection properties of the epoxy coating on the steel substrate. The mixture of silanes, especially those containing higher content of APS, caused the greatest improvement in the adhesion properties of the epoxy coating on the steel surface. APS contains NH_2 groups which could produce covalent bonds with the epoxide groups of the epoxy coating.

References

[1] Saravanan G, Mohan S. Corrosion behavior of Cr electrodeposited from Cr(VI) and Cr(III)-baths, using direct (DCD) and pulse electrodeposition (PED) techniques. Corros Sci 2009;51:197–202.
[2] Niu LY, Li GY, Jiang ZH, Sun LP, Han D, Lian JS. Influence of sodium metanitrobenzene sulphonate on structures and surface morphologies of phosphate coating on AZ91D. Trans Nonferr Met Soc China 2006;16(3):567–71.
[3] Ramezanzadeh B, Attar MM, Farzam M. Corrosion performance of a hot-dip galvanized steel treated by different kinds of conversion coatings. Surf Coat Technol 2010;205:874–84.
[4] Ramezanzadeh B, Vakili H, Amini R. The effects of addition of poly(vinyl) alcohol (PVA) as a green corrosion inhibitor to the phosphate conversion coating on the anticorrosion and adhesion properties of the epoxy coating on the steel substrate. Appl Surf Sci 2015;327(1):174–81.
[5] Sherif El-S. M. Corrosion inhibition in 2.0 M sulfuric acid solutions of high strength maraging steel by aminophenyl tetrazole as a corrosion inhibitor. Appl Surf Sci 2014;292(15):190–6.
[6] Jin ZH, Ge HH, Lin WW, Zong YW, Liu SJ, Shi JM. Corrosion behaviour of 316L stainless steel and anti-corrosion materials in a high acidified chloride solution. Appl Surf Sci 2014;322(15):47–50.
[7] Kowsari E, Payami M, Amini R, Ramezanzadeh B, Javanbakht M. Task-specific ionic liquid as a new green inhibitor of mild steel corrosion. Appl Surf Sci 2014;289(15):478–86.
[8] Ramezanzadeh B, Arman SY, Mehdipour M, Markhali BP. Analysis of electrochemical noise (ECN) data in time and frequency domain for comparison corrosion inhibition of some azole compounds on Cu in 1.0 M H_2SO_4 solution. Appl Surf Sci 2014;289(15):129–40.
[9] Conradi M, Kocijan A, Kek-Merl D, Zorko M. Verpoest I. Mechanical and anticorrosion properties of nanosilica-filled epoxy-resin composite coatings. Appl Surf Sci 2014;292(15):432–40.
[10] Murillo-Gutiérrez NV, Ansart F, Bonino J-P, Kunst SR, Malfatti CF. Architectural optimization of an epoxy-based hybrid sol–gel coating for the corrosion protection of a cast Elektron magnesium alloy. Appl Surf Sci 2014;309(1):62–6.
[11] Palimi MJ, Rostami M, Mahdavian M, Ramezanzadeh B. Surface modification of Fe_2O_3 nanoparticles with 3-aminopropyltrimethoxysilane (APTMS): an attempt to investigate surface treatment on surface chemistry and mechanical properties of polyurethane/Fe_2O_3 nanocomposites. Appl Surf Sci 2014;320(30):60–72.
[12] Liu X, Xiong J, Lv Y, Zuo Y. Study on corrosion electrochemical behavior of several different coating systems by EIS. Prog Org Coat 2009;64:497–503.
[13] Ramezanzadeh B, Attar MM. An evaluation of the corrosion resistance and adhesion properties of an epoxy-nanocomposite on a hot-dip galvanized steel (HDG) treated by different kinds of conversion coatings. Surf Coat Technol 2011;205(19):4649–57.
[14] Lee YL, Chu YR, Chen FJ, Lin CS. Mechanism of the formation of stannate and cerium conversion coatings on AZ91D magnesium alloys. Appl Surf Sci 2013;276(1):578–97.
[15] Sharifi Golru S, Attar MM, Ramezanzadeh B. Morphological analysis and corrosion performance of zirconium based conversion coating on the aluminum alloy 1050. J Ind Eng Chem, 2015;24:233–44.
[16] V. Gentil Corrosion, LTC 3rd ed.; Rio de Janeiro; 1987: pp. 319–384.
[17] Jegannathana S, Sankara Narayanan TSN, Ravichandrana K. Formation of zinc–zinc phosphate composite coatings by cathodic electrochemical treatment. Surf Coat Technol 2006;200:4117–26.
[18] Morks MF. Magnesium phosphate treatment for steel. Mater Lett 2004;58(3316):1100–6.
[19] William Adrian B, Kurt G. Chromate rinse for phosphate coated metals and metal products; US3864175 A ;1975.
[20] Xue D, Van Ooij WJ. Corrosion performance improvement of hot-dipped galvanized (HDG) steels by electro-deposition of epoxy-resin-ester modified bis-[tri-ethoxy-silyl]ethane (BTSE) coatings. Prog Org Coat 2013;76:1095–102.
[21] Certhoux E, Ansart FE, Turq V, Bonino PJ, Sobrino MJ, Garcia J, Reby J. New sol–gel formulations to increase the barrier effect of a protective coating against the corrosion of steels. Prog Org Coat 2013;76:165–79.
[22] Verma PC, Colreavy J, John C, Oubaha M, Duffy B, McDonagh C. Effect of organic chelates on the performance of hybrid sol–gel coated AA 2024-T3 aluminium alloys. Prog Org Coat 2009;66:406–11.
[23] Phanasgaonkar A, Raja VS. Influence of curing temperature, silica nanoparticles- and cerium on surface morphology and corrosion behaviour of hybrid silane coatings on mild steel. Surf Coat Technol 2009;203(16):2260–71.
[24] Singh Raman R, Balan P, et al. Effect of nanoparticle addition in hybrid sol–gel silane coating on corrosion resistance of low carbon steel. Adv Mater Res 2013;686:244–9.
[25] Naderi R, Fedel M, Deflorian F, Poelman M, Olivier M. Synergistic effect of clay nanoparticles and cerium component on the corrosion behavior of eco-friendly silane sol–gel layer applied on pure aluminum. Surf Coat Technol 2013;224(15):93–102.
[26] Fedel M, Poelman M, Zago M, Vandermiers C, Cossement D, Olivier M-G, Deflorian F. Influence of formulation and application parameters on the performances of a sol–gel/clay nanocomposite on the corrosion resistance of hot-dip galvanized steel. Part II. Effect of curing temperature and time. Surf Coat Technol 2015;274:9–17.

[27] May M, Wang HM, Akid R. Effects of the addition of inorganic nanoparticles on the adhesive strength of a hybrid sol–gel epoxy system. Int J Adhes Adhes 2010;30(6):505–12.

[28] Meyer S, Schubert U, De Bardi M, Wiesinger R, Schreiner M, Grohmann T. Adhesion pretreatment of aluminum by sol–gel processing. Int J Adhes Adhes 2014;51:103–10.

[29] Lei W, Chang-sheng L, Hai-yun YU, Cheng-qiang AN. Structure and corrosion resistance of a composite γ-amino propyltriethoxy silane and γ-glycidoxy propyl trimethoxy silaneconversion coating on galvanized steel. J Iron Steel Res Int 2012;19(11):46–51.

[30] Deflorian F, Rossi S, Fedel M, Motte C. Electrochemical investigation of high-performance silane sol–gel films containing clay nanoparticles. Prog Org Coat 2010;69:158–66.

[31] Li D, Neumann AW. A reformulation of the equation of state for interfacial tensions. J Colloid Interface Sci 1992;137:304–7.

[32] Kumar Ghosh A, Bertelsb E, Goderis B, Smet M, Van Hemelrijck D, Van Mele B. Optimisation of wet chemical silane deposition to improve the interfacial strength of stainless steel/epoxy. Appl Surf Sci 2015;324:134–42.

[33] Arkles B. Silane coupling agents: connecting across boundaries; Gelest; Morrisville; 2006, 〈http://www.gelest.com/_〉 [accessed 20.5.14].