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Molybdate-doped sulfonated-polyaniline (SPni.Mo) grafted CNT nano-particles for fabrication of a dual-functional epoxy composite coating with durable corrosion resistance function

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Abstract

Carbon nanotubes nano-particles modified with organic-inorganic hybrid inhibitors, i.e., sulfonated polyaniline doped with molybdate (OMC.SPni.Mo) was designed to improve the anti-corrosion capability of carbon nanotubes for application in an epoxy polymer coating. The ability to release the inhibitors from the OMC.SPni.Mo surface in the saline solution at different pHs was demonstrated by EIS and ICP techniques. Epoxy resin reinforced with this nanohybrid, (OMC.SPni.Mo.EPoxy) was applied to the steel plate. EIS test outcomes revealed that after 90 days of immersion, the OMC.SPni.Mo.EPoxy sample did not show a significant change in the $\text{Log}|Z|_{10\text{mHz}} (\geq 10.5 \Omega\text{cm}^2)$. The OMC.SPni.Mo.EPoxy coating active corrosion mitigation after scratching was evaluated by the EIS technique and accelerated salt spray test. In this case, the total resistance reached $106.200 \Omega\text{cm}^2$, which is 118% more than the pure coating. The improvement of the coating resistance is due to the film development in the scratched area and the prevention of corrosive agents from reaching the metal surface. The enhancement of the barrier protection against the progress of harmful ions in the coating-substrate interface and the adhesion of the OMC.SPni.Mo.EPoxy coating to the substrate compared to the sample coated with epoxy was presented by cathodic delamination and pull-off tests.

Keywords: Corrosion, Active protection, Carbon nanotube Nano-particle, Epoxy coating

1. Introduction

The polymer coating is considered a simple and conventional solution to protect steel against corrosion. Epoxy coating with good chemical and mechanical properties and high adhesion to the metal substrate is one of the most widely used polymers [1–3]. Researchers have attempted to develop the performance of this coating by using different strategies and innovative routes. Loading fillers and pigments with special capabilities (mechanical, chemical, thermal, anti-corrosion, self-healing, etc.) into epoxy coatings has led to a significant improvement in their properties [4–8]. Therefore, by loading fillers or pigments as an inhibitor or barrier agent with special capabilities in epoxy coatings, its characteristics have been modified and accompanied by significant improvement [9–11].

Conductive polymer like polyaniline (PANI) has been used in various applications due to their uncomplicated synthesis, non-toxicity, environmental permanence, and good conductive properties. Therefore, its anti-corrosion capability by creating a barrier against harmful corrosive ions and forming a passive film (reversible transition between the oxidation and reduction states of polyaniline) on the metal has been presented in various studies [12–15]. Hydrophobicity and agglomeration in water-based coatings and inappropriate adhesion to the substrate are considered major disadvantages of PANI, which adversely affect the corrosion resistance performance. Therefore, researchers have tried to overcome these drawbacks by using different solutions i.e., using aniline derivatives, copolymerizing aniline with other monomers, and the selection of appropriate dopants and surfactants [16–19]. Yang et al. [20] and Qiu et al. [21] created sulfonated polyaniline (SPani) as one of polyaniline derivatives through copolymerization. The corrosion protection capability of the coating with a small

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amount of SPani is enhanced by SPani self-doping and creating a resistance oxide layer on the steel substance.

In addition, by creating PANI-based nano-particles with inorganic or organic inhibitors, the anti-corrosion capacity of the coating can be enhanced. Jin et al. [22] prepared and applied the coating containing PANI-pyrrole-molybdate copolymer on the steel substrate. Examination of the corrosion-blocking behavior of the coating illustrated that the creation of a protective layer under anodic protection has improved the active resistance of the coating. Situ and co-workers [23] synthesized polyaniline-titanium nitride (PANI-TiN) nano-particle and presented the improvement of the anti-corrosion ability of epoxy coating modified with this nano-hybrid by a mixed mechanism, “passivation - labyrinth effect”. Do et al. [24] prepared Sulfonated polyaniline/Mg-Al layered double hydroxides hybrid nano-particles and loaded them into epoxy coatings. They revealed that increasing the barrier capability and creating a passive layer are two reasons for the enhancement of the nano-filler-loaded epoxy film resistance against corrosion. Ahadiparsa and co-workers [25] synthesized MXene/SPni/Zn nanofiller and by loading them into the epoxy coating indicated a great barrier resistance increase.

The approach of using nano-particles, especially carbon-based nanomaterials in different types, dimensions, and shapes in the epoxy coating has enhanced its corrosion-blocking behavior [26–28]. The unique characteristics of carbon nanotubes (CNT), such as high specific surface area, storage capability, and noble properties (mechanical, electrical, and thermal) have led to the use of these nanomaterials in the polymeric coatings as reinforcement, fillers, containers, and carriers, which has increased its adhesion strength and anti-corrosion protection [29–33]. Kumar and Gasem [34] synthesized the nano-particle of functionalized CNT and PANI and after applying it to the steel substrate, they showed an increase in its corrosion protection ability. Najmi et al. [35] synthesized a nano-particle containing a multi-walled

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carbon nanotube (MWCNT) with PANI doped with zinc and created a self-healing and anti-corrosion coating system by applying it to the epoxy coating.

Since MWCNT has a low active protection capability in polymer coating systems, the main innovation of this work is to raise the active protection capacity of the coating by loading the modified carbon nanotubes doped with inhibitors. On the other hand, investigating the corrosion-blocking performance of using two inhibitors at the same time (SPni and molybdate as organic and inorganic inhibitors, respectively) in the epoxy coating is considered another aim of this study. For this purpose, after the synthesis and characterization of nano-particles, they were applied to the epoxy coating, and their anti-corrosion performance, blocking resistance, and active protection (self-healing) were studied by electrochemical methods, salt spray, cathodic disbondment, and pull-off tests.

2. Experimental activities

2.1. Materials

The aniline monomers, nitric acid, hydrochloric acid 37%, sulfuric acid 98%, and amino benzene sulfonic acid (95%) were supplied from Sigma-Aldrich Co. (USA). Ammonium peroxodisulfate and 4-aminodiphenyl-amine were provided by Merck Co. (Germany). Sodium molybdate dehydrates were supplied by Kernel Chemical Co. (China). The MWCNT (wall number = 3–15 nm and length = 1–10 μm) and epoxy resin (EP-R) and polyamide hardener (PA-H) were provided from Nanostartech and Saba Chem Co. (Iran), respectively. The st-12 steel plate with the composition of 0.12 wt% C, 0.3 wt% Si, 0.05 wt% Sn, 0.045 wt% P, 0.5 wt% Mn and 93.3 wt% Fe was received from Foolad Mobarakeh Co. (Iran) and cut into $10 \times 8 \times 0.2$ cm dimensions.

2.2. Prepared nano-particles

At first, MWCNT was functionalized with carbon groups under the oxidation process. In this situation, suitable reactive sites are created on the MWCNT to reach a proper distribution and bonding with epoxy and other inhibitors. To prepare the oxidized MWCNT (OMC), after preparing an acidic solution including sulfuric acid and nitric acid (ratio of 3:1), 1 g of MWCNT was added to it and placed under mixing at a temperature of 150 °C for 24 h. The diluted solution containing OMC was centrifuged several times with HCl/H₂O. Finally, the OMC nano- particle was prepared after drying the collected centrifuged product in an oven at 70 °C for 24 h.

Sulfonated polyaniline (SPi) was first grafted on the oxidized nanotube by in situ polymerization to reach OMC.SPni nano-particle. For this aim, 0.2 wt% (50 mg) of OMC nano-particles was inserted into 1 M HCl solution (16.5 ml) containing monomers of aniline (150 mg) and aminobenzene sulfonic acid (150 mg) under stirring. 4-amino diphenylamine (7.5 mg) as a catalyst to accelerate the polymerization process ammonium sulfate peroxide (300 mg) was inserted into the solution as a polymerization agent and the solution was kept at ambient temperature for 24 h to complete the polymerization process. Finally, in order to remove free monomers from the OMC surface, the solution was washed with deionized water.

The OMC.SPni nano-particles were mixed in deionized water and to homogenize them in the solution, then it was exposed to sonication for several minutes. On the other hand, the aqueous solution containing 500 mg of sodium molybdate dehydrates (as the second inhibitor) is combined with the solution containing the OMC.SPni nano-particles. The solution was placed under stirring for 3 h and after washing twice with deionized water, the OMC.SPni.Mo nano-particle was created.

2.3. Fabrication of modified epoxy coatings with nano-particle

In order to modify the epoxy coating, 0.2 wt% of nano-particle was inserted into epoxy resin (22.6 g) and placed under mixing for 5 h. After ensuring uniform distribution and no agglomeration of nano-particle in the resin, a hardener (17.4 g) was added to the resin. After polishing the surface of steel plates with sandpaper and then washing them with acetone, the epoxy coating without nano-particle (EPoxy) and epoxy coatings modified with nano-particles (OMC.EPoxy, OMC.SPni.EPoxy, OMC.SPni.Mo.EPoxy) were coated on the steel plates. Finally, the samples were placed in the oven (80 °C, 120 min) for curing prior tests. The thickness of the coatings for electrochemical impedance spectroscopy (EIS), salt spray, pull-off, and cathodic delamination tests is considered equal to $60 \pm 3 \mu\text{m}$, $80 \pm 3 \mu\text{m}$, $105 \pm 5 \mu\text{m}$, and $90 \pm 5 \mu\text{m}$, respectively.

2.4. Characterisation tests

Investigation of the chemical structure of the fabricated nanoparticles was done by Fourier transform infrared (FT-IR) (Avator model, Termo, USA) and Raman (Xplora Plus model, Horiba Scientific, France) spectroscopies. The elemental composition and the different phases related to the nano-particles were identified by X-ray diffraction (XRD) with a Cu-K α radiation source and a limited angle of 6–80° (PW1730 mode, Philips, Netherlands). The evaluation of the thermal characteristics of nano-particles was done using thermogravimetric analysis (TGA) in the temperature range of 50–550 °C in N₂ gas (Q600, TA, USA). Observing the surface morphology of nano-particles and the product created at the scratch area of the coating have been studied by FE-SEM/ EDS, (Mira3 LMU, Tescan, Czech Republic).

2.5. Corrosion tests

Inductively coupled plasma optical emission spectroscopy (ICP-OES) test with Varian 720/730-ES was used to measure the released mineral inhibitor ions (molybdate anions) concentration from OMC.SPni.Mo nano-particle. Therefore, 1 g nano-particle was inserted into saline solutions (3.5 wt% NaCl) with pHs of 3, 6, and 12. After stirring for 12 h, the solutions containing OMC.SPni.Mo extract was centrifuged and 10 ppm of each solution was used for the ICP-OES test. The corrosion resistance of the nano-particles (barrier and active resistance) in the corrosive environment in two phases, “solution and coating”, was investigated by EIS analysis.

At the 10,000–0.01 Hz range of frequency, the EIS test was implemented with iVium compact compactstat instrument (Netherlands) under sinusoidal voltage (amplitude of 10 mV). Also, in the solution phase, the polarization test was used at a potential of ± 0.2 V and with a recording speed of 0.001 V/s.

In the solution phase, after preparing 3.5 wt% NaCl solutions containing 0.1 g of nano-particle extract, the surface of 1×1 cm² of the steel plates were exposed to the solution and evaluated for 48 h. In the coating phase, the surface of the coated sample without a scratch (intact) and with an artificial scratch (in dimensions of 1×1 cm² and 2×2 cm², respectively) was subjected to saline solution in the periods of 90 days and 48 h, respectively.

The active protection capacity of the epoxy coatings modified with nano-particles was investigated by a salt spray test [36]. To perform this test, a 3×3 cm² surface of the coated samples (with artificial scratch) was examined during 120 days in contact with the corrosive environment. The ability to prevent the passage of harmful agents to the metal-coating interface of the samples in corrosive media was investigated using the cathodic delamination test. Therefore, according to the ASTM G 8–96 standard [37], the surface of the coated samples

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with defects (an artificial hole with $D = 4$ mm was created in the center of the circle) was immersed in salt solution and subjected to cathodic protection potential, and after 24 h, the delamination of the coatings was measured.

The adhesion capability of the prepared coatings to the steel plate has been evaluated with the dry and wet pull-off test (ASTM D 4541 standard [38]). Therefore, aluminum dollys were attached to the surface of the coated sample and after 24 h, the dollys were pulled (pull speed = 10 mm/min). The pull-off was also operated after soaking the samples in 3.5% NaCl solution for three weeks to investigate wet adhesion.

3. Results and discussion

3.1. Characterization

3.1.1. FT-IR and Raman analysis examination

The information extracted from FT-IR and Raman analysis to examine and compare the chemical structure of the prepared nanoparticles was demonstrated in Fig. 1. The peaks appearing in the FT-IR plots of the nano-particles were identified by examining the researchers' studies and the results were presented. The creation of the O–H bond in the spectrum of OMC and OMC.SPni samples are related to the remaining water molecules in the nano-particles [39]. Also, in these plots, the OMC stretching vibration bonds (C=O, C–O, and C–H) can be seen almost unchanged [31,40]. In OMC.SPni plot, adsorption of sulfonated polyaniline on carbon nanotube with the appearance of C=C bond peaks of the quinonoid ring and benzenoid ring at 1632 cm^{-1} and 1429 cm^{-1} are indicated, respectively [41,42]. The appearance of the peaks related to Mo–O and Mo=O bonds in the spectrum of OMC.SPni. Mo confirms the bond of molybdate with the surface of OMC.SPni [43, 44].

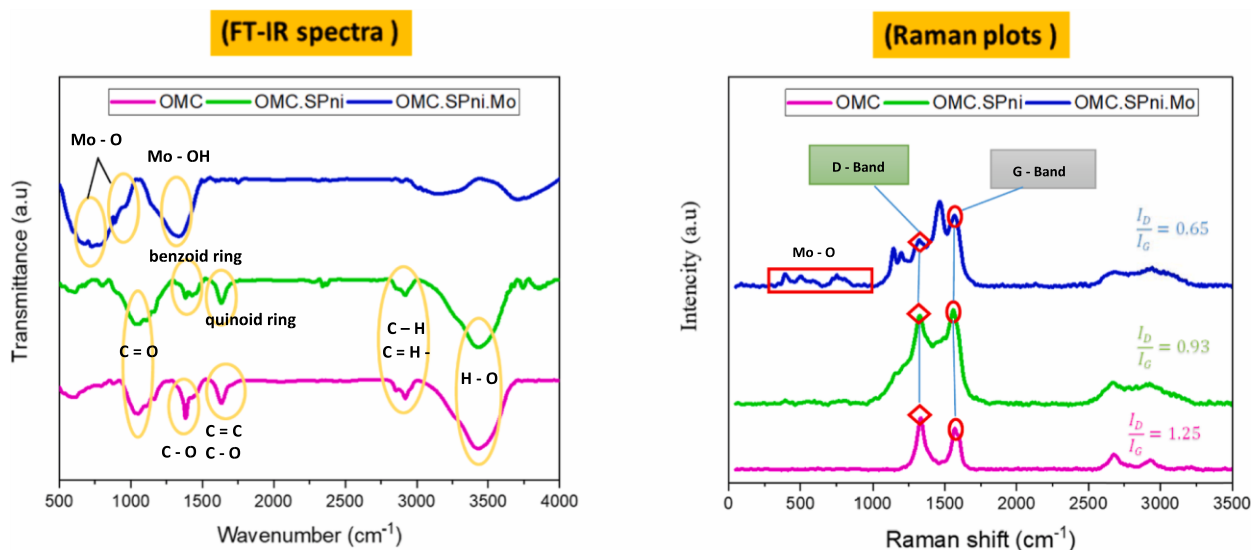


Fig. 1. FT-IR and Raman plots of prepared Nano-particles.

In the Raman plots of samples, two important peaks of the D & G- band related to CNT can be seen in the wavelength extent of $1320\text{--}1330\text{ cm}^{-1}$ and $1560\text{--}1570\text{ cm}^{-1}$, respectively. The grafting of SPni on the OMC caused the appearance of peaks at the wavelengths of 1169 cm^{-1} and 1260 cm^{-1} , 1464 cm^{-1} of spectrum OMC.SPni and OMC.SPni.Mo, which describes the C–H of the quinoid ring (QR) and benzenoid ring (BR), and the C=N of the QR [18]. In the spectrum of OMC.SPni.Mo with the appearance of peaks at the wavelengths of 393 cm^{-1} , 502 cm^{-1} , 587 cm^{-1} , and 753 cm^{-1} , the absorption of MoO_2 on the OMC surface can be well recognized [45,46]. As shown in the figure, by loading each of the inhibitors on the OMC, the I_D/I_G ratio has reduced, which confirms the absorption of the inhibitors on the MWCNT [18,47].

3.1.2. XRD and TGA analysis

The structure of the fabricated nanoparticles was characterized using XRD analysis and the plots of the samples are presented in Fig. 2. The peak appearing in $2\theta = 25.8^\circ$ is observed in all three curves, which corresponds to the (200) plane of CNT and the intensity of this peak

(212)

decreased by loading inhibitors on OMC [48]. In the OMC.SPni plot, the peaks with an insignificant intensity related to the amorphous structure of sulfonated polyaniline have appeared in the range $2\theta = 15\text{--}23^\circ$, which indicates the adsorption of this inhibitor on OMC [49]. The interaction of the molybdate ions with the surface of sulfonated polyaniline and carbon nanotube will lead to the formation of the MoO_2 compound on the surface of the nanoparticle. In the OMC.SPni.Mo plot, the peaks located at $2\theta = 31.89^\circ$ and 43.29° are correspond to the (111) and crystal planes of MoO_2 , respectively [45,50].

The thermal characteristics of synthesized nano-particles have been investigated by presenting TGA curves in Fig. 3 and the amount of weight loss of the samples is shown in Table 1. The evaporation of water molecules in the synthesized samples was reduced by 5–10% in the range of $50\text{--}100^\circ\text{C}$. All samples experienced weight loss in the range of $350\text{--}550^\circ\text{C}$. The degradation of OMC in this range is very intense and therefore the weight loss of this sample is approximately 65%, which is caused by the decomposition of carboxylic acid and amide groups formed on the surface of oxidized MWCNT. Examining the TGA results of the OMC.SPni and OMC samples in the temperature range of $350\text{--}550^\circ\text{C}$ show a decrease in weight percentage of approximately 10%. The greater weight loss of the OMC.SPni diagram in this temperature range indicates the decomposition of sulfonated polyaniline from the OMC surface. Therefore, this weight loss can be related to the amount of sulfonated polyaniline inhibitor absorbed on the nanoparticles' surface.

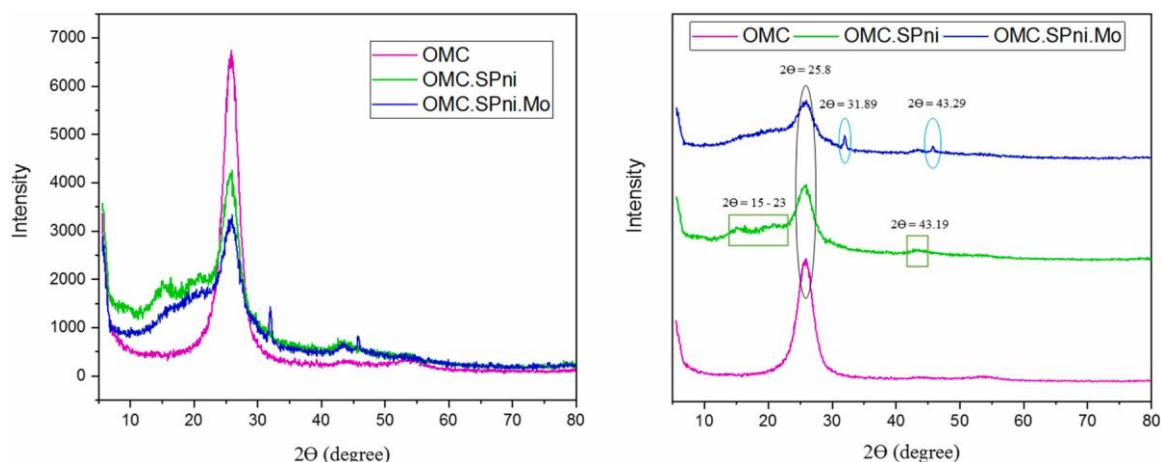


Fig. 2. XRD curves of OMC, OMC.SPni and OMC.SPni.Mo nanoparticles.

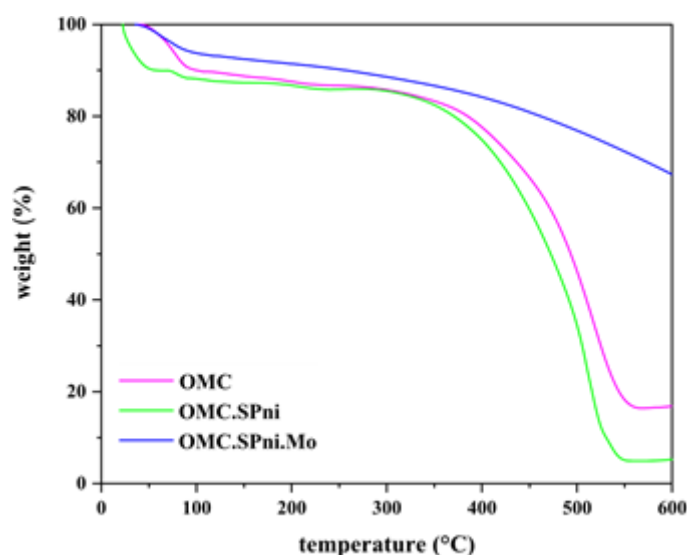


Fig. 3. TGA plots of OMC, OMC.SPni and OMC.SPni.Mo nanoparticles.

Table 1. The amount of weight loss of synthesized nanoparticles in different temperature ranges.

Sample	Weight loss (%)		
	0–100 (°C)	100–350 (°C)	350–550 (°C)
OMC	10	16.3	81.7
OMC.SPni	11.5	16.4	91.5
OMC.SPni.Mo	6.3	13.4	28.7

The adsorption of the two inhibitors on the OMC surface has increased the thermal stability of OMC.SPni.Mo nano-particles compared to OMC. The TGA results of all three samples show that the addition of molybdate inhibitor in the OMC.SPni.Mo sample is directly effective in increasing the thermal stability of the nanoparticles. The weight loss in OMC.SPni.Mo sample up to the temperature of 550 °C was done with a very soft slope, which at this temperature was reported as 28.7%. Due to the mineral nature of molybdate, the binding of this inhibitor with SPni and OMC leads to the formation of complexes and MoO₂ on the surface and increases the stability of nanoparticles against heat. Also, the weight difference between OMC.SPni.Mo and OMC diagrams in the temperature range of 350–550 °C indicate the volume fraction (about 50%) of the inhibitors absorbed on the OMC surface.

3.1.3. Investigating the microscopic structure of the nano-particles

The microscopic structure of the surface of the synthesized nanoparticles was investigated by FE-SEM/EDS (Fig. 4). The absorption of inhibitors on the oxidized nanotubes has increased the thickness and roughened the surface. The adsorption of molybdate inhibitor on the OMC.SPni can be clearly seen in the image, which causes its partial agglomeration and accumulation. Also, the absorption of the inhibitors can be clearly seen by the color changes shown in the EDS map, and the detection of peaks related to Mo, S, and N elements in the results of EDS plots confirms the deposition of inhibitors on the surface of OMC. On the other hand, the interaction of sulfonated polyaniline with OMC has decreased the amount of oxygen, but by loading molybdate into OMC. SPni nano-particle, molybdate bonded with oxygen (formation of MoO and MoOH products) and increased the amount of molybdate and oxygen, which is evident in the EDS results.

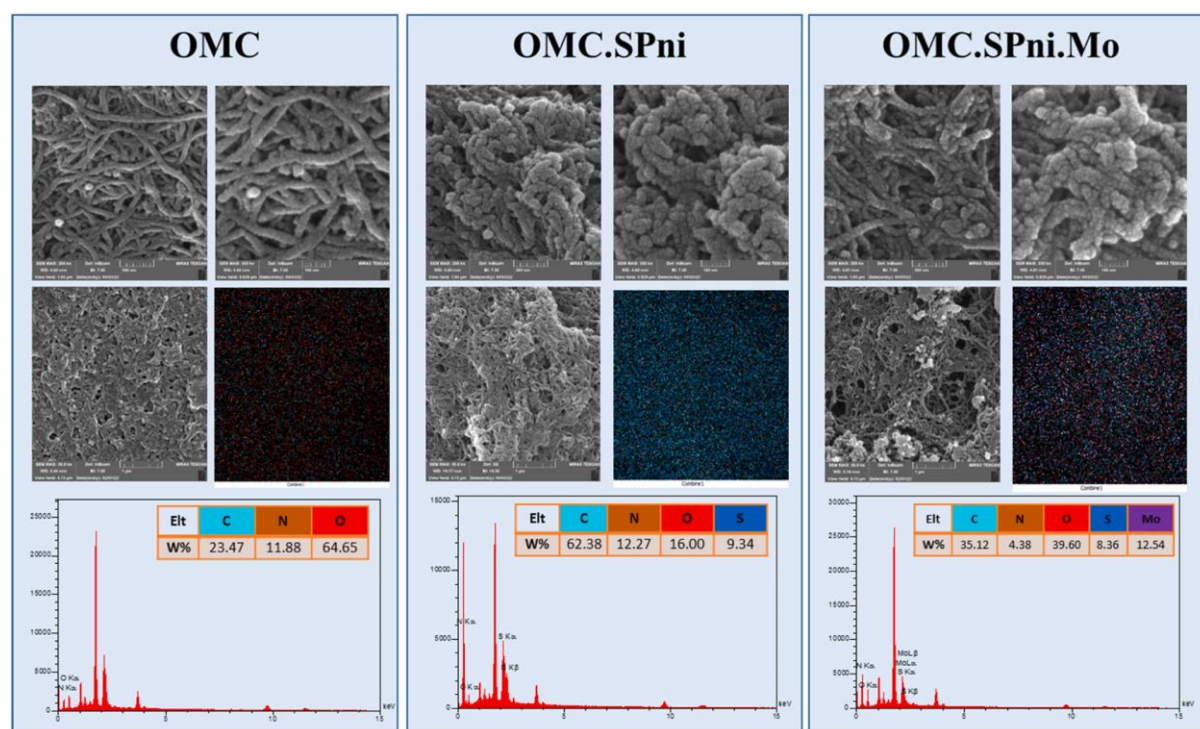


Fig. 4. Nyquist plots of steel plates soaking in saline solution without/with prepared nano-particles extracts in the solution phase.

3.2. Corrosion protection study

3.2.1. The ability to release nano-particles

The ICP-OES analysis was used to ensure the absorption of molybdate (MoO_4^{2-}) inorganic inhibitor on OMC.SPni nano-particle and its release capability. For this purpose, the OMC.SPni.Mo nano-particle was added to 3.5% NaCl solution at different pHs (natural, acidic, and alkaline solutions) and after stirring for 24 h, the extract was evaluated. The amount of molybdate released at pH 3, 7, and 12 was 4.8, 11, and 11.8 ppm, respectively. According to the obtained results, molybdate inhibitor absorption and its ability to release from OMC.SPni.Mo nano-particle in different environments were confirmed.

In order to know about the release capability of inhibitors and the anti-corrosion ability of the prepared nano-particles, the inhibitory behavior of the nano-particles in the solution phase

has been investigated. For this purpose, 3.5% NaCl solutions with the extract of nano- particles (OMC.SPni and OMC.SPni.Mo) were prepared and the surface of the steel plate ($1 \times 1 \text{ cm}^2$) was exposed to these solutions. Their corrosion inhibition performance during 48 h was evaluated and compared by EIS analysis and Nyquist diagram (Fig. 5 and Table 2). Also, a saline solution without extract (Blank) was prepared and analyzed to evaluate and compare the inhibitory behavior of the nano- particles. It should be mentioned that the diagrams were fitted with Z- Simp software using one-constant and two-constant equivalent circuits.

Table 2. EIS data of steel plates soaked in saline solution with/without nano-particles extract.

Sample	Immersion time (h)	R_T ($\Omega \text{ cm}^2$)	CPE_{dl} ($\mu\Omega^{-1} \text{ cm}^2 \text{ s}^n$)		R_{ct} ($\Omega \text{ cm}^2$)	CPE_c ($\mu\Omega^{-1} \text{ cm}^2 \text{ s}^n$)		R_c ($\Omega \text{ cm}^2$)	R_s ($\Omega \text{ cm}^2$)
			n	Y_0		n	Y_0		
Blank	1	1034	0.8	130	1034	—	—	—	11.54
	3	1225	0.8	460	1225	—	—	—	8.52
	5	1330	0.8	337	1330	—	—	—	7.82
	24	1798	0.8	230	1798	—	—	—	7.14
	48	1590	0.75	306	1590	—	—	—	7.09
OMC.SPni	1	1256	0.8	251.5	1256	—	—	—	7.44
	3	1667	0.6	213.9	1667	—	—	—	8.19
	5	2199	0.8	189.2	2199	—	—	—	7.88
	24	1430	0.8	172.5	1430	—	—	—	9.02
	48	2193	0.8	166.1	2193	—	—	—	7.44
OMC.SPni.Mo	1	1104	0.8	47	1311	0.8	161	1099	9.91
	3	1212	0.8	150	917.5	1	372	294.3	9.22
	5	1365	0.8	143	1011	1	301	354	8.40
	24	2152	0.8	182	1636	0.9	10^{-9}	516	4.04
	48	2792	0.8	156	2094	1	349	698	6.95

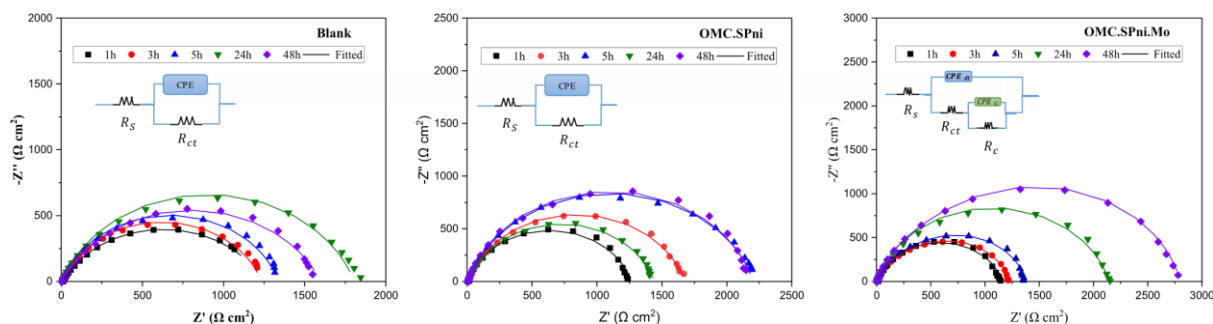


Fig. 5. Nyquist plots of steel plates soaking in saline solution without/with prepared nano-particles extracts in solution phase.

The enhancement of the Nyquist diagram loops diameter for OMC. SPni.Mo after 24 h of immersion indicates the release of molybdate and sulfonated polyaniline inhibitors. The total resistance (R_T) of OMC.SPni. Mo sample after 48 h of immersion has been significantly increased, so the R_T has improved by 27% and 75% compared to the OMC.SPni and Blank samples, respectively. The reaction of molybdate negative ions with Fe^{2+}/Fe^{3+} and the creation of the Leuco-Emeraldine form of PANI increases the anti-corrosion performance by forming a stable layer on the surface.

Potentiodynamic polarization plots and results of the samples soaked in saline solution without and with nano-particles extract are shown in Fig. 6 and Table 3. The enhancement in potential (E_{corr}) and reduction of the corrosion current (i_{corr}) of the OMC.SPni.Mo indicates the high anti-corrosion capability of the designed nano-particle. So that the inhibition efficiency and polarization resistance (R_p) of this sample have increased by 35% and 34%, respectively compared to the Blank sample. The noticeable decrease in the slope of the anodic branch of samples OMC. SPni and OMC.SPni.Mo is due to the influence of sulfonated polyaniline and molybdate inhibitors in anodic protection and the corrosion has been controlled. In addition to the mentioned cases, the simultaneous presence of the inhibitor and carbon nanotubes in the prepared nano-particle has also been effective in the cathodic reactions and has increased the

cathodic Tafel slope. Finally, the addition of these nano- particles to the coating under a mixed protection mechanism (cathodic and anodic protection) will control corrosion.

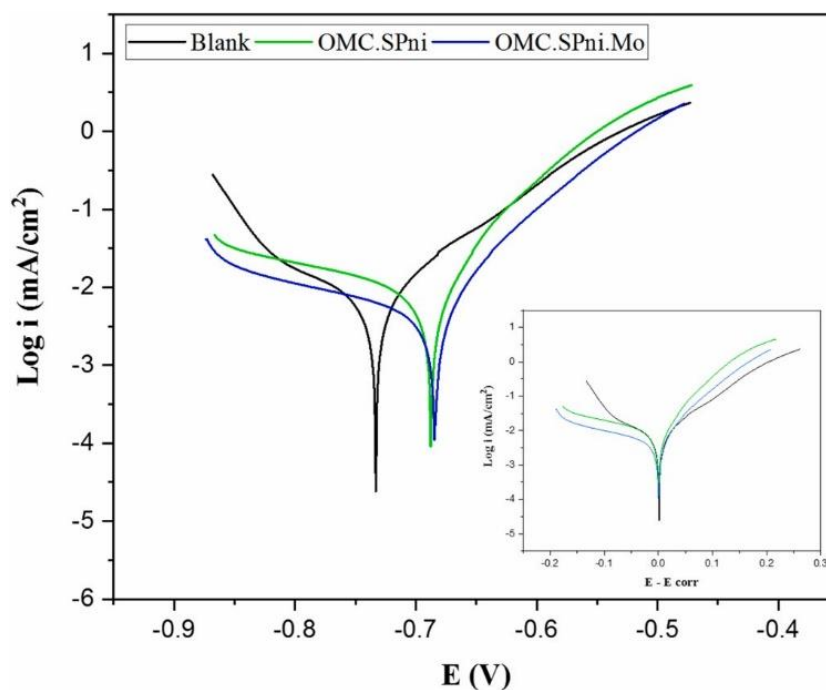


Fig. 6. Polarization plots of mild steel samples soaked in Saline solution without and with OMC.SPni and OMC.SPni.Mo extracts after 48 h soaked.

Table 3. Polarization test results of samples after 48 h immersion in saline solution.

Sample	Unit	Blank	OMC.SPni	OMC.SPni.Mo
corrosion potential (E_{corr})	V	-0.734	-0.694	-0.684
corrosion current (i_{corr})	$\mu\text{m} / \text{cm}^2$	6.317	9.15	4.072
resistance polarization (R_p)	ohm.cm^2	3692	2374	4971
anodic brench (β_a)	V/dec	0.084	0.060	0.057
anodic branch ($-\beta_c$)	V/dec	0.15	0.296	0.246

The steel plate surface was probed after 48 h of immersion in the saline solutions with/ without the nano-particle extracts and was examined by FE-SEM/EDS (Fig. 7). The surface of the plate was exposed to OMC.SPni extract is covered with a smooth and dense protective layer. On the other hand, the protective film is created on the surface of the plate in contact

with the OMC.SPni.Mo extract has changed significantly compared to OMC.SPni and become denser and rougher. In the results of EDS mapping, the existence of sulfur and nitrogen elements in the OMC.SPni sample, and the presence of molybdate and the reduction of oxygen and nitrogen in OMC.SPni.Mo indicated the release of inhibitors from the nano-particle and the reaction with the metal surface.

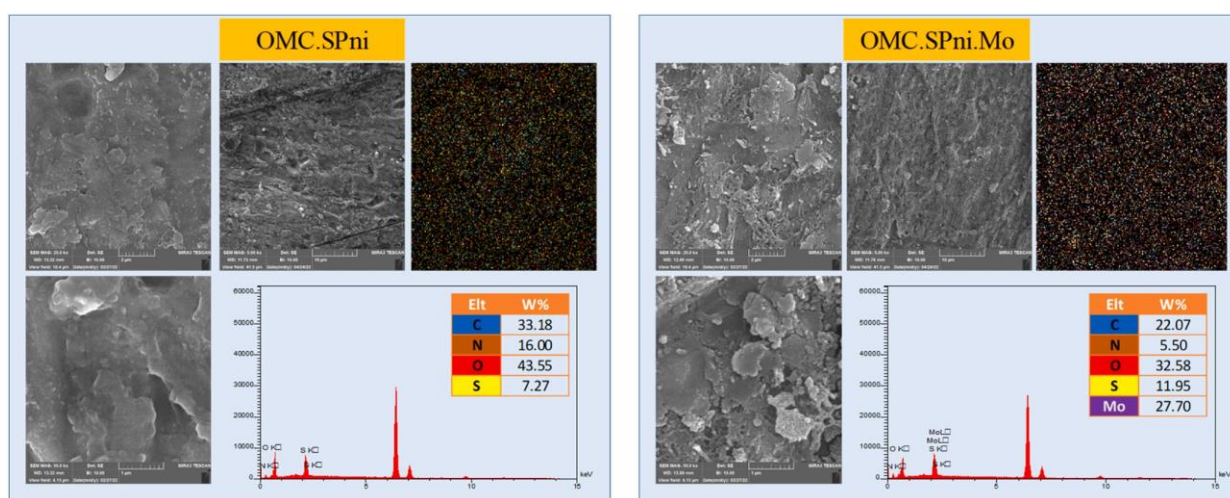


Fig. 7. FE-SEM and EDS mapping images of the surface of steel plates after 48 h of immersion in saline solution containing extract OMC.SPni and OMC.SPni.Mo.

The FT-IR spectra of the steel plate immersed in the saline solution containing the extract of OMC.SPni and OMC.SPni.Mo nano-hybrids are presented in Fig. 8. Examining the major peaks screened in the FT-IR spectra shows the presence of adsorbed inhibitor film on the metal surface caused by the reaction of the released inhibitors with the iron ions in the corrosive environment and the metal surface. Several peaks are detected at 3444, 2920, 2850, 1695, 1630, 1385, 1033, and 719 cm^{-1} , which are attributed to OH, CH_2 , CH_3 , $\text{C}=\text{N}$, $\text{C}=\text{C}$, COOH , $\text{C}-\text{N}$ and $\text{Fe}-\text{O}$, respectively. Also, in the OMC.SPni.Mo spectrum, the peaks recorded at 586 cm^{-1} and in the range of 700–1000 cm^{-1} are related to $\text{Mo}-\text{O}$ and $\text{Fe}^{2+}-\text{MoO}_4^{2-}$ complex, respectively,

which indicates the successful deposition of molybdate inhibitor on the sample surface [35,51,52].

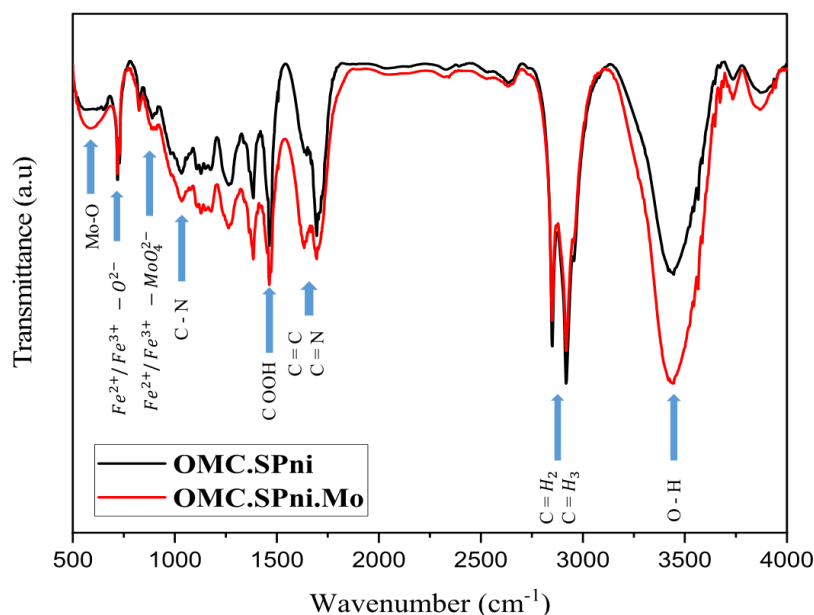


Fig. 8. FTIR spectra of the film formed on the steel plate immersed in saline solution containing OMC.SPni, OMC.SPni.Mo extracts.

3.2.2. Anti-corrosion ability of the epoxy coating modified with nano- particles

3.2.2.1. EIS study. Loading the prepared nano-particles into the epoxy coating and applying each of them on the steel plate can influence the barrier resistance ability of the coatings, so it has been investigated by EIS analysis. After immersing the coated samples in saline solution for a period of time (90 days), the EIS plots of the EPoxy, OMC.EPoxy, OMC.SPni.EPoxy and OMC.SPni.Mo.EPoxy coatings are obtained and presented in Figs. 9 and 10, respectively.

A significant expansion in the inhibitory corrosion-blocking performance of the modified coatings in the short period of immersion is due to the barrier capacity of nano-particles, which is clearly visible in the plots. The EPoxy coating barrier function decreases after 30 days, while

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other samples have shown good stability against corrosive agents and their $\text{Log}|Z|_{(10 \text{ mHz})}$ has shown more than $10.5 \Omega\text{cm}^2$. The breaking point frequency (f_b) of less than 0.01 Hz of the samples OMC.EPoxy, OMC.SPni.EPoxy and OMC.SPni.Mo.EPoxy during the test period indicates the absence of corrosive ions in the interface.

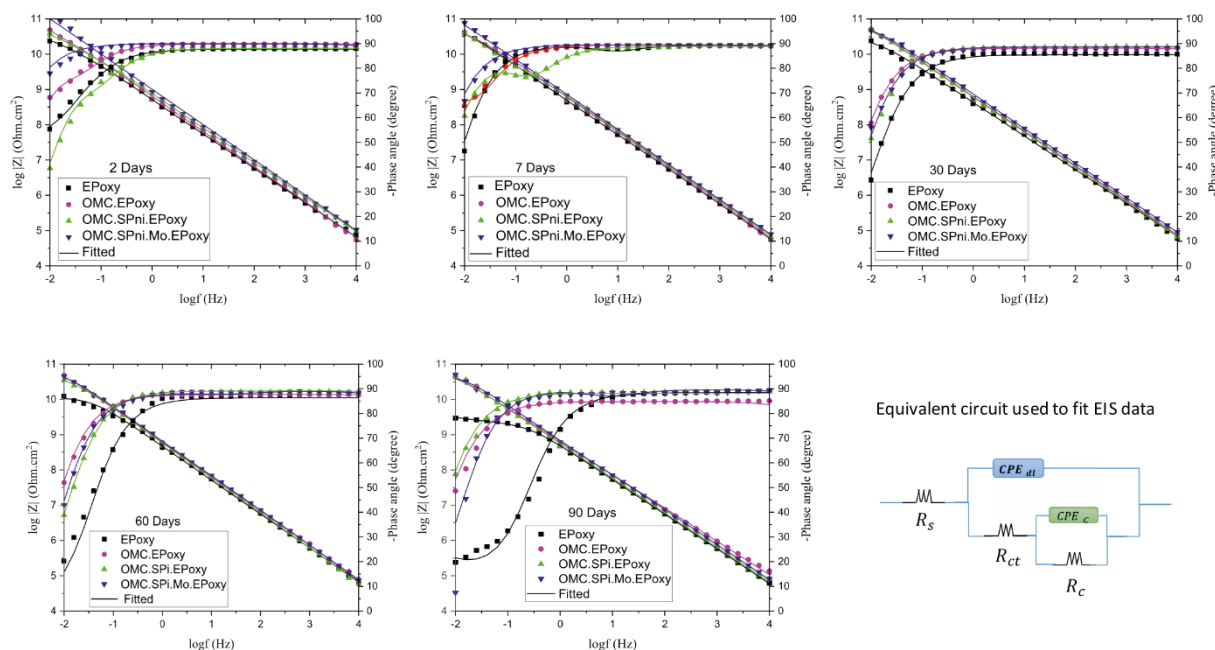


Fig. 9. Bode plots of steel plates coated with EPoxy, OMC.EPoxy, OMC.SPni.EPoxy and OMC.SPni.Mo.EPoxy coatings after 2, 7, 30, 60 and 90 days of immersion in 3.5% NaCl solution.

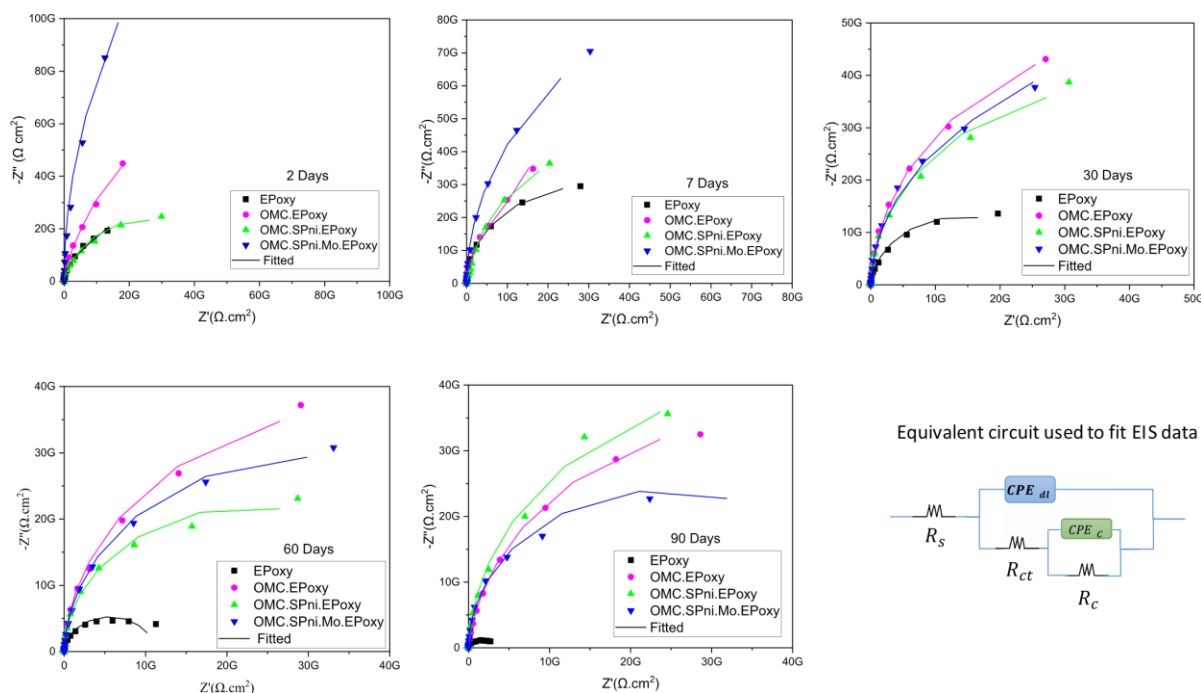


Fig. 10. Nyquist plots of steel plates coated with prepared coatings during 90 days' immersion in saline solution.

Examination of Nyquist plots has shown that the high reactivity of molybdate inhibitor with free cations in the coating in the first days of immersion has increased the charge transfer resistance ($R_{ct} = 195.7 \text{ G}\Omega \text{ cm}^2$) of OMC.SPni.Mo.EPoxy compared to other samples. With the passage of time (90 days of immersion), the active resistivity of OMC. SPni.Mo.EPoxy decreased and the total resistance reached a value of $48.2 \text{ G}\Omega \text{ cm}^2$, while the total resistance of the OMC.SPni.EPoxy reached a higher level ($R_T = 82 \text{ G}\Omega \text{ cm}^2$). The increase in the coating resistance of this sample was caused by the release of polyaniline and its reactivity with corrosive ions and the creation of a protective film in the coating.

The active resistance capacity of the modified epoxy coatings was estimated by EIS analysis after scratching the coatings and immersing them in a saline solution for 48 h. EIS plots of the coated plates in each time period are presented separately in Fig. 11 and the related parameters are listed in Table 4.

Table 4. The result of EIS analysis of EPoxy, OMC.EPoxy, OMC.SPni.EPoxy and OMC.SPni.Mo.EPoxy coatings with scratch immersed in 3.5% NaCl solution.

Sample	Immersion time (h)	$-\theta_{10\text{kHz}}$ (Degree)	$\text{Log} Z _{10\text{mHz}}$ ($\Omega \text{ cm}^2$)	R_T ($\Omega \text{ cm}^2$)	CPE_{dl} ($\mu\Omega^{-1} \text{ cm}^{-2} \text{ s}^n$)		R_{ct} ($\Omega \text{ cm}^2$)	CPE_c ($\mu\Omega^{-1} \text{ cm}^{-2} \text{ s}^n$)		R_c ($\Omega \text{ cm}^2$)	R_s ($\Omega \text{ cm}^2$)
					n	Y_0		n	Y_0		
EPoxy	1	5.79	4.59	39,577	0.83	0.43	37,060	0.6	0.14	2517	0.097
	3	6.94	4.79	59,165	0.80	8.52	2285	0.80	0.17	56,880	114.4
	5	6.38	4.76	56,697	0.73	0.20	5097	1	0.32	51,600	110.7
	24	5.23	4.83	63,430	0.72	0.11	440.3	0.68	0.17	62,990	110.1
	48	9.21	4.69	48,660	0.60	0.26	21,170	0.74	0.30	27,490	95.8
OMC.EPoxy	1	8.96	4.88	79,257	0.80	8.19	407.4	0.77	4.34	78,850	92.45
	3	5.92	5.01	110,564	0.84	7.89	964.9	0.72	5.33	109,600	105.7
	5	7.26	4.93	897,045	0.79	0.10	545.2	0.77	2.68	896,500	102.9
	24	9.2	4.72	59,440	1	0.31	0.01	0.64	0.22	59,440	125.9
	48	10.3	4.68	60,582	0.75	8.44	2142	0.57	29	58,440	126.5
OMC.SPni.EPoxy	1	12.5	4.72	63,856	0.66	24	1896	0.81	14.6	61,960	95.41
	3	4.29	4.91	102,790	0.75	25.9	2090	0.82	15.8	100,700	108.1
	5	5.22	4.95	118,936	0.72	30.8	5036	0.9	8.28	113,900	102.1
	24	8.07	4.73	69,037	0.68	23.9	2207	0.66	8.32	66,830	117.5
	48	12.2	4.60	59,669	0.59	39.4	5139	1	0.01	54,530	114.7
OMC.SPni.Mo.EPoxy	1	14.2	4.76	70,192	0.69	17.5	62,790	1	0.01	7402	83.5
	3	5.75	5.02	117,918	0.79	12.5	110,400	1	4	7518	111.8
	5	9.06	5.01	112,576	0.76	8.03	76.76	0.8	4.4	112,500	100.9
	24	12.1	4.97	103,288	0.72	11.4	387.5	0.71	2.78	102,900	110.8
	48	14.6	4.96	106,200	0.66	16.4	58,060	0.98	6.13	48,140	110.4

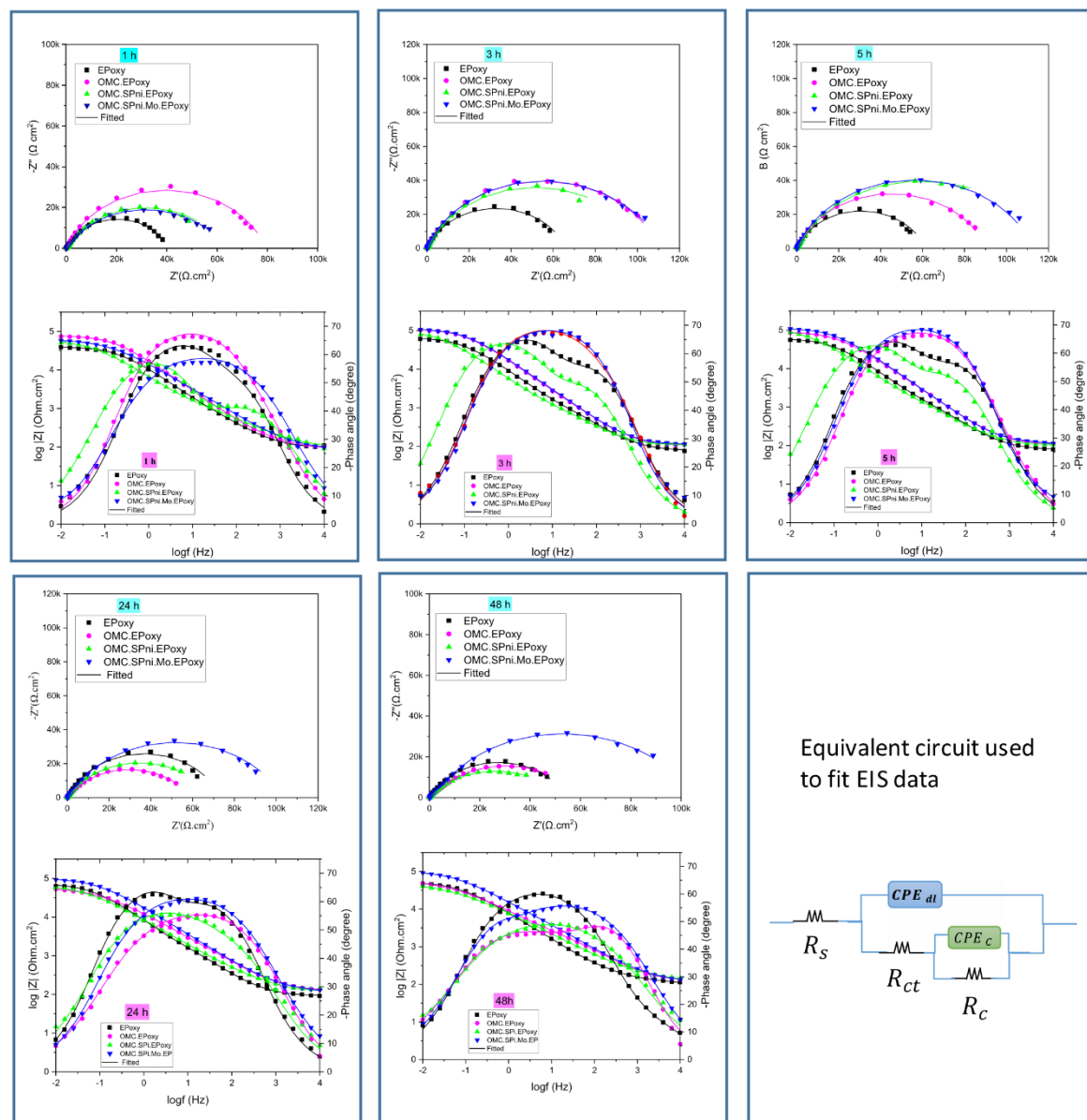


Fig. 11. Nyquist and Bode plots (top and bottom of each box, respectively) of coated samples with an artificial scratch at different immersion times in 3.5% NaCl aqueous solution.

Penetration of corrosive agents into the scratch area will cause a reaction with the free ions of the metal surface, causing corrosion progression and lessening the coating protection ability, which is well seen in the results obtained from the EPoxy sample. In the scratched area of the coatings containing nano-particles, the nano-particles reacted with the corrosive agents in this area and repair the scratch area by forming a passive film. The speed of reaction and the ability

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to release inhibitors at the scratch site in the presence of corrosive agents have a remarkable effect on the active resistance and self-healing of the coating. The rapid reactivity of molybdate with Fe cations and H^+ absorption has increased the charge transfer resistance of OMC.SPni.Mo.EPoxy coating from the first hours of immersion ($R_{ct} = 110,400 \Omega$ at 3 h of immersion) and with the creation of reaction products, a protective film will be formed at the scratch area. After 48 h of immersion, the R_T of this sample is equal to $106,200 \Omega \text{ cm}^2$, which is 118%, 75%, and 77% higher than EPoxy, OMC. EPoxy and OMC.SPni.EPoxy samples, respectively. The increase in $\text{Log}|Z|$ at low frequency (10 mHz) and $-\theta$ at high frequency (10 kHz) of OMC.SPni.Mo.EPoxy compared to other samples confirms the proper active performance of this sample.

Also, the FE-SEM/EDS images of the scratch site are presented in Fig. 12 to evaluate the products formed in this area. Investigative images have shown that a film is created in the scratch area of OMC.SPni.Mo. EPoxy sample which according to the severity of the reactivity of the inhibitors, the amount of corrosion products in these samples is at its minimum level. On the other hand, the EDS results confirm the release of inhibitors in the scratch area by showing molybdate and sulfur atoms in the scratch zone.

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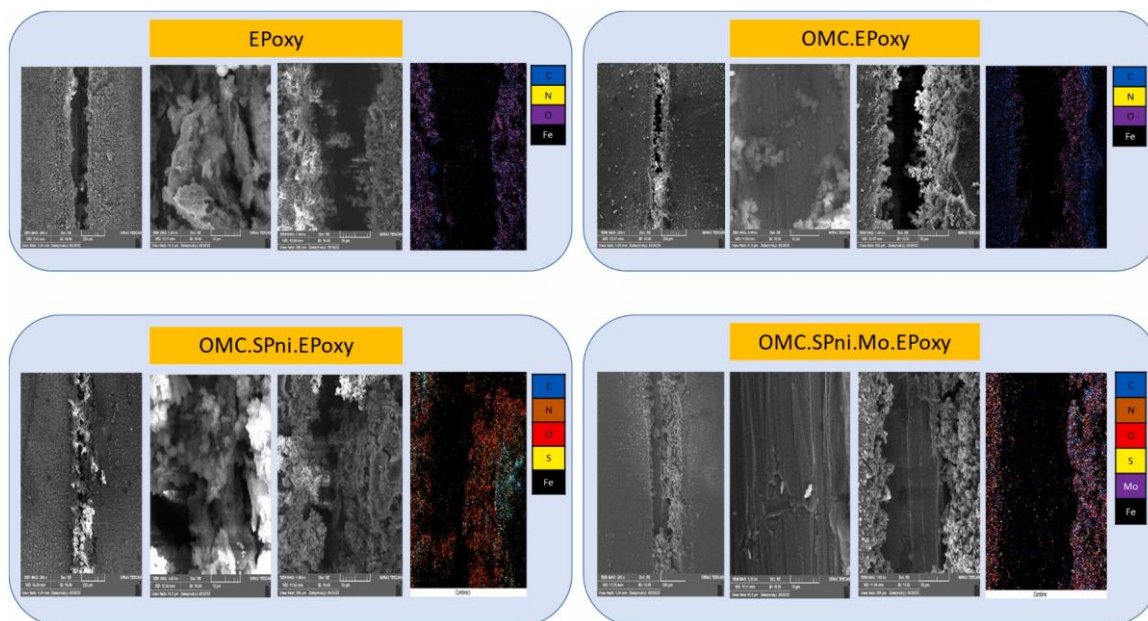


Fig. 12. SEM and EDS mapping image of the scratch area of samples after 48 h of immersion in 3.5% NaCl solution.

As shown schematically in Fig. 13, the nano-particles fill the pores and defects of the epoxy coating and increase the path of corrosive ions to the substrate thus improving the barrier protection. Also, the inhibition ability of the nano-particles prevents corrosion during chemical reactions with metal ions and corrosive ions under the process of active protection. The coating's inhibitive potency against corrosion attacks is because of the inhibitors (molybdate and sulfonated polyaniline) and OMC presence and their very suitable synergistic effectiveness against corrosive agents.

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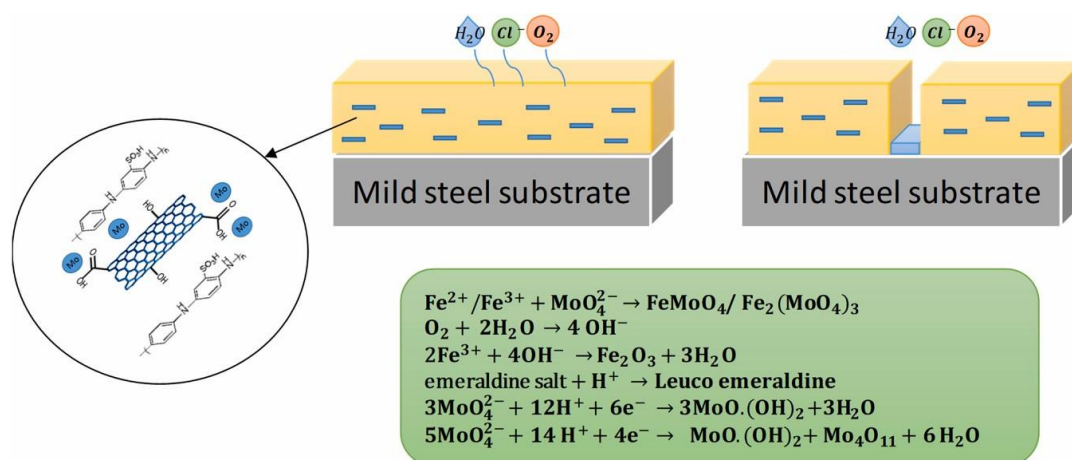


Fig. 13. Schematic of the corrosion resistance mechanism of the OMC.SPni.Mo.EPoxy sample against corrosive agents.

3.2.2.2. Salt spray. The active resistance and self-healing capability of the coated samples with scratch during 120 days of exposure to harmful corrosive ions were evaluated under the salt spray test (Fig. 14). In the first days of the test, the corrosive agents quickly penetrate into the scratch area and react with the surface of the metal or coating. The instability of the products formed in this area causes the progress of corrosive ions into the interface, and as a result, it causes failure and delamination of the coating. This process is well visible in samples of EPoxy and OMC.EPoxy, so that the coating has failed after 60 and 90 days, respectively. While the protective layer formed in OMC.SPni. EPoxy and OMC.SPni.Mo.EPoxy samples remained almost unchanged after 120 days and prevented the progress of harmful corrosive agents into the coating–substrate interface and provided very good barrier protection. Also, the lower thickness of the repaired area in these samples shows their high self-healing ability (active protection) compared to the epoxy sample, which shows the performance of inhibitors in the coating system.

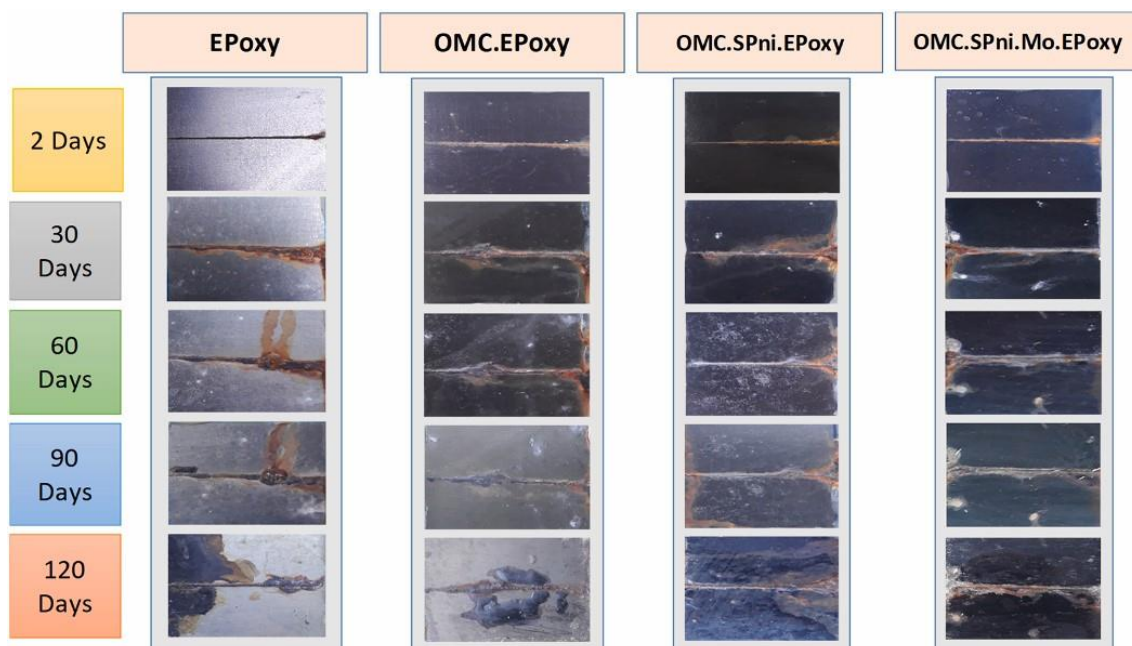


Fig. 14. Images of the scratch area of the coatings in the salt spray test after 120 days.

3.2.2.3. Cathodic delamination test. The barrier protection of the samples at the coating-substrate boundary and its resistance against harmful corrosive agents has been investigated via the cathodic delamination test during 24 h in saline solution (3.5% NaCl) under a potential of -1.5 V. Improving the bonding of nano-particle-modified epoxy coatings with the substrate increases adhesion and prevents the progress of harmful ions into the joint boundary. The diameter of the coating separated from the metal surface of the modified epoxy coatings is reduced as shown in Fig. 15. So the decrease in the diameter of OMC. SPni.Mo.EPoxy is 16% less than the EPoxy sample. The active protection capability of OMC.SPni.EPoxy and OMC.SPni.Mo.EPoxy coatings can also reduce the diameter of disbanding of the coatings due to the participation of inhibitors on the anodic or cathodic zones.

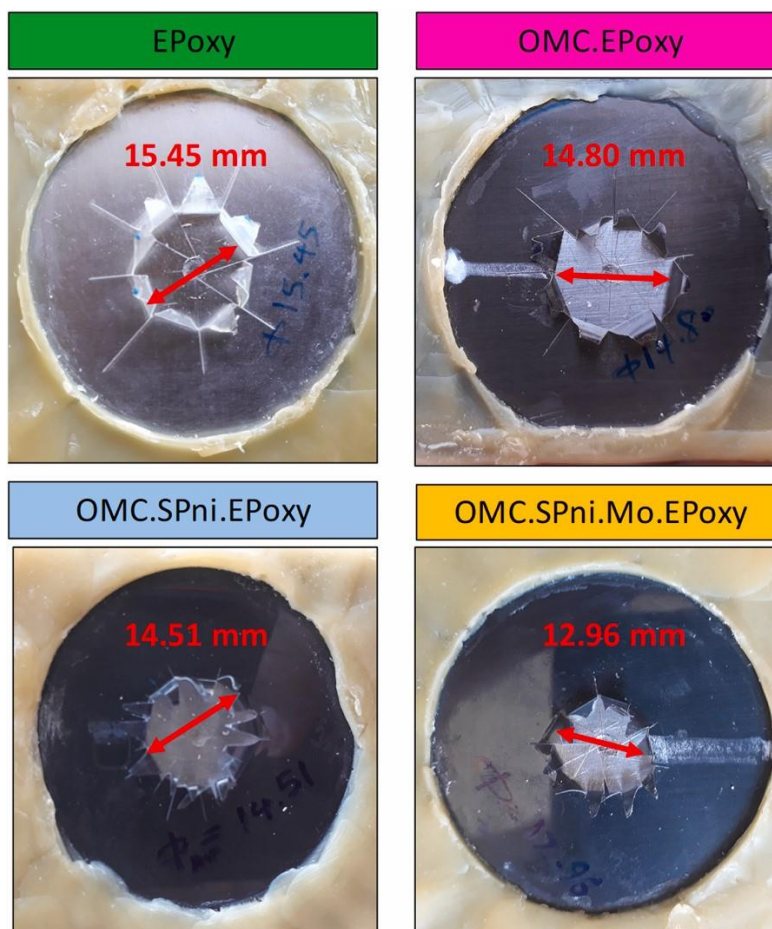


Fig. 15. Cathodic delamination test of coated steel plate.

3.2.2.4. Adhesion of modified coatings. The coating's ability to bond with the metal surface (substrate) and prevent the progress of harmful ions at the interface was evaluated by the pull-off method and the results are presented in Fig. 16. The modified MWCNT in the coating have increased the active contact surface of the coating with the substrate and improved the adhesion of the coating. Also, the OMC modified with inhibitors has also reduced penetration into the coating. Therefore, after 3 weeks of immersing the samples in saline solution, the loss of strength in the modified epoxy samples decreased. The adhesion performance of OMC.EPoxy and OMC.SPni.EPoxy coatings are almost similar to each other, but with the addition of molybdate inhibitor, the adhesion performance of OMC.SPni.Mo.EPoxy coating has improved

significantly. Therefore, the strength loss percentage of the OMC.SPni.Mo.EPoxy sample was 9%, which is 78% better than the EPoxy sample.

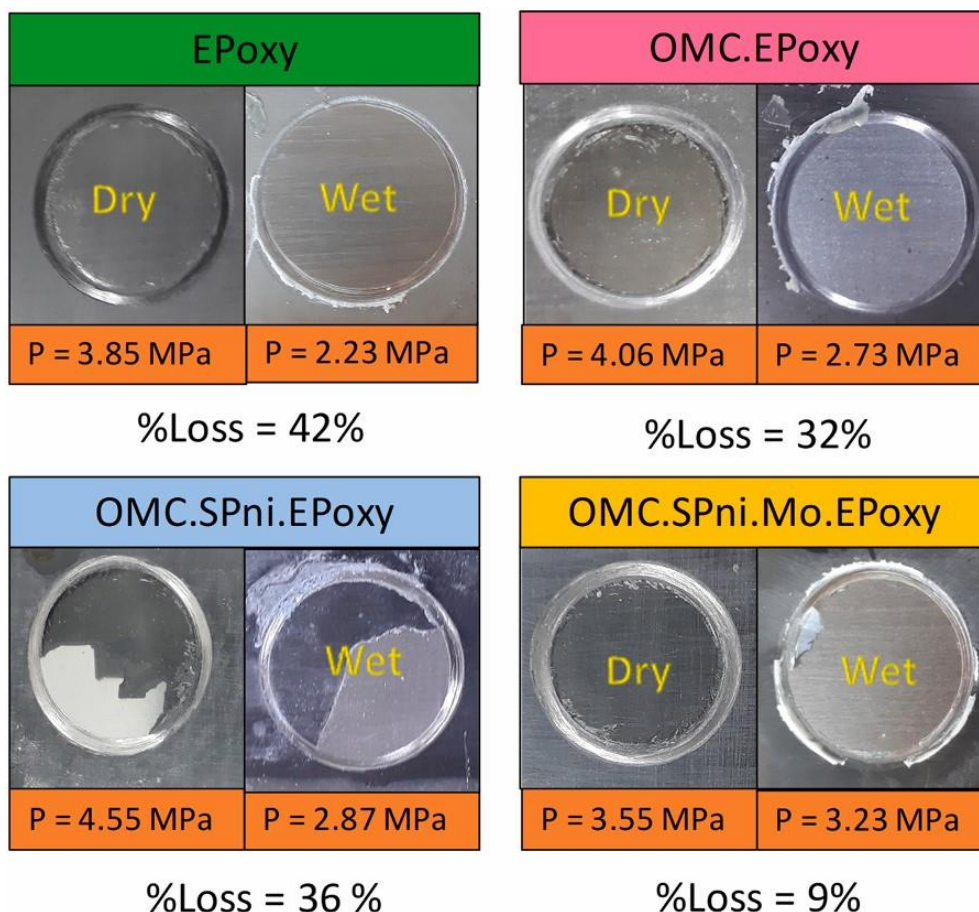


Fig. 16. The result of Pull – off (dry – wet) test.

3.3. Comparative studies

The anti-corrosion ability of the coating system modified with synthesized nanoparticles in this work is compared with some similar studies and the results are summarized in Table 5. In these studies, the researchers have applied the synthesized nanoparticles in the polymer coating and evaluated the anti-corrosion capability of the coating after immersion in the corrosive solution. The review of similar studies shows the great corrosion resistance of the epoxy coating modified with OMC. SPni.Mo nanoparticles. As can be seen from this table, the

loading of carbon-based nanoparticles decorated with organic and inorganic inhibitors will significantly improve the anti-corrosion properties of the coating. By adding a small amount of this type of nanoparticles to the coating, the barrier resistance of the coating has increased. In this case, the reported $\log |Z|$ (at low frequency) value is higher than those reported in literature even at longer immersion times. The proper distribution and reactivity of OMC.SPni.Mo nanoparticles to the coating and substrate have improved the anti-corrosion properties and prevented the penetration of corrosive agents into the coating system.

Table 5. Comparative table about anti-corrosion studies of polymeric coatings reinforced with carbon-based nanoparticles doped with organic or inorganic inhibitors.

Sample name	Additive (%wt)	Type of coating	Corrosive ambience	Immersion time	Coating Thickness (μm)	Summary of results	Year
Porous silica-GO-MoO ₄	0.15	polyvinyl butyral	3.5% NaCl	21 days	50 $\pm$ 3	$\text{Log} Z _{10\text{mHz}} = 10.1 \Omega\text{cm}^2$	2019 [53]
GO-PANI	0.3	Epoxy	3.5% NaCl	618 h	55 $\pm$ 3	$\text{Log} Z _{10\text{mHz}} = 10.6 \Omega\text{cm}^2$	2018 [54]
rGO-SPANI	1	Epoxy	3.5% NaCl	30 days	55 $\pm$ 5	$ Z _{10\text{mHz}} = 4.0 \text{ M}\Omega\text{cm}^2$	2019 [16]
GO-PANI-Zn	0.2	Epoxy	3.5% NaCl	77 days	68 $\pm$ 5	$\text{Log} Z _{10\text{mHz}} > 8.5 \Omega\text{cm}^2$	2019 [55]
GO-PDA-MoO ₄	0.15	Epoxy	3.5% NaCl	70 days	70 $\pm$ 5	$\text{Log} Z _{10\text{mHz}} = 10 \Omega\text{cm}^2$	2023 [46]
GO-Polypyrrole-MoO ₄	0.2	Epoxy	3.5% NaCl	56 days	70 $\pm$ 5	$\text{Log} Z _{10\text{mHz}} = 10.50 \Omega\text{cm}^2$	2022 [56]
CNT/CaCO ₃ - PANI	1	Epoxy	3.5% NaCl	29 days	30	$\text{Log} Z _{10\text{mHz}} = 5.17 \Omega\text{cm}^2$	2020 [57]
CNT/LDH-MoO ₄	4	Epoxy	3.5% NaCl	60 days	100 $\pm$ 10	$\text{Log} Z _{10\text{mHz}} = 11.2 \Omega\text{cm}^2$	2021 [58]
MWCNT-PANI-Zn	0.15	Epoxy	3.5% NaCl	70 days	70	$\text{Log} Z _{10\text{mHz}} = 10.3 \Omega\text{cm}^2$	2021 [35]

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MWCNT- SPANI-MoO ₄	0.2	Epoxy	3.5% NaCl	90 days	57 ± 3	$\text{Log} Z _{10\text{mHz}} =$ $10.70 \Omega\text{cm}^2$	present work
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4. Conclusion

Carbon nanotubes modified with organic-inorganic hybrid inhibitors, i.e., sulfonated polyaniline doped with molybdate (OMC.SPni. Mo) was produced and characterized by doped organic-inorganic inhibitors consisting of sulfonated polyaniline and molybdate anions on the surface of an oxidized multi-walled carbon nanotube. The ability of active protection and barrier resistance of this nano-particle against corrosive agents in the solution phase and after loading into the epoxy coating on a steel plate has been investigated with different methods and the important derived results are mentioned below:

1. The total resistance, inhibition efficiency, and polarization resistance of the steel plate soaked in a 3.5% NaCl solution containing OMC. SPni.Mo nano-particle extract has increased by 75%, 35%, and 34% respectively compared to the steel plate soaked in 3.5% NaCl solution without nano-particle extract for 48 h (In the solution phase).
2. The ability to release molybdate inorganic inhibitors from the nano- particle surface under pH changes was shown. The amount of molybdate released in the neutral and alkaline environments was reported to be almost three times higher than in the acidic environment.
3. The addition of OMC.SPni.Mo nano-particles to the epoxy coating (OMC.SPni.Mo.EPOxy) have led to a significant enhancement in the barrier protection of the coating up to 90 days of immersion of the coated samples in the 3.5% NaCl solution.
4. The higher impedance values OMC.SPni.Mo.EPOxy compared to other samples after 48 h of soaking confirms the proper performance of active protection of this coating by a passive protective layer creation.
5. The active protection and self-healing capability of the OMC.SPni. Mo.EPOxy sample with scratch was well demonstrated during 120 days of exposure to harmful corrosive ions.

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6. The improved barrier protection of the OMC.SPni.Mo.EPOxy sample at the coating-substrate boundary and its higher resistance against the progress of corrosive agents compared to the sample coated with epoxy were presented in the cathodic delamination test.
7. The increase in the adhesion of the OMC.SPni.Mo.EPOxy sample to the substrate surface was well demonstrated in the pull-off (dry and wet) test. So that the strength loss percentage of the OMC.SPni.Mo. EPOxy sample was reported to be 78% less than the sample coated with epoxy.

CRedit authorship contribution statement

Hamid Jalali: Writing – original draft. **Reza Eslami-Farsani:** Writing – review & editing. **Bahram Ramezanzadeh:** Writing – review & editing.

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.

Data availability

The data that has been used is confidential.

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