RESEARCH PAPER

Self-Healing and Anti-Corrosion Nanocomposite Coatings Based on Polyurethane Nanocapsules containing Mercapto Benzimidazole

Omid Razaghi Kashani [1], Sahar Amiri [1] and Mariam Hosseini Zori [2]*

[1] *Department of Polymer Engineering, Science and Research Branch, Islamic Azad University, Tehran, Iran*

[2] *Department of Inorganic Pigments and Glazes, Institute for Color Science and Technology (ICST), Tehran, Iran*

ABSTRACT

Self-healing and anti-corrosion nanocomposites were synthesized using polyurethane nanocapsules loading with 2-mercaptobenzimidazole (MBI) as an anti-corrosion agent. Polyurethane nanocapsules were synthesized using toluene diisocyanate and propanediol interfacial polymerization in an emulsion solution. The resulting nanocapsules were characterized using FTIR, SEM, and EDX. The polyurethane nanocapsules were added to a silane hybrid sol-gel coating, and the coating structure, anti-corrosion, and self-healing performance of the obtained coatings were evaluated using electrochemical and accelerated standard tests. SEM results indicate a uniform dispersion of PU nanocapsules and successful particle synthesis. The size of the nanoparticles was below 100 nm. The mechanical performance of the self-healing coating layer was analyzed by a pull-off adhesion test to determine compatibility with a commercially-available resin epoxy topcoat system. Meanwhile, a long-term 3000-hour salt spray and 4200-hour cyclic UV test were used to determine the self-healing coating's durability under extreme environments. EIS results showed that polyurethane nanocapsules improve the coatings' active corrosion protection. A pull-off test was also performed on the samples, indicating the coatings' good surface adhesion.

How to cite this article
Razaghi Kashani O, Amiri S, Hosseini Zori M. Self-Healing and Anti-Corrosion Nanocomposite Coatings Based on Polyurethane Nanocapsules containing Mercapto Benzimidazole. J Nanostruct, 2022; 12(3):726-737. DOI: 10.22052/ JNS.2022.03.025

INTRODUCTION

Many methods have been applied to design smart coatings based on urethane capsules loaded with active ingredients. They are released by creating cracks in the healing agent's coating, thereby healing the coating [1]. Organic silica-based coatings prepared using the sol-gel method in the presence of organic corrosion inhibitors protect the surface against corrosion. The coating requires an active corrosion inhibitor to improve its anti-corrosion properties subjected to mechanical damage. In this regard, organic corrosion inhibitors are suitable solutions for producing anti-corrosion coatings [2,3].

Self-healing materials are a class of intelligent products that are structurally capable of fixing damaged parts on their own and over their useful life or production. A microcapsule loaded with anti-corrosion active agents was applied into epoxy resin. The catalyst was detached

* *Corresponding Author Email: s.amiri@srbiau.ac.ir*

from the ruptured microcapsule shells at a high temperature. Self-healing coatings can enhance the system's operational performance while extending its service life by saving time, money, and downtime [4-6].

Microencapsulation is a technology that is frequently employed in self-healing applications. It involves dispersing nanocapsules containing healing chemicals in a trapped condition through a passive coating matrix. Microencapsulation is a frequently employed technology in self-healing applications for damaged coating surfaces. It involves dispersing nanocapsules containing healing chemicals in a trapped condition through a passive coating matrix. Polyurethane (PU) nanocapsules are widely utilized in self-healing composites due to their compatibility with various materials and high adhesion to various substances [3,7].

Additionally, the polyurethane shell is controllable due to the wide range of possible modifications in polyurethane synthesis. The healing process proceeds from the reaction between the hydroxyl and isocyanate groups in the polyurethane resin (released from the ruptured nanocapsules) and the hardener. However, the nanocapsules' self-healing ability and efficiency must be enhanced. Notably, polyurethane nanocapsules may be compatible with polyurethane coating systems and exhibit high adherence to the polyurethane coating matrix. Thiazole and triazole derivatives are effective corrosion inhibitors for AA2024 due to their chemisorption properties in copper-rich intermetallic particles and have been encapsulated in a range of inorganic and polymeric reservoirs, including polyurethane [8-10].

Self-healing and corrosion-resistant coatings were created in this study by encapsulating MBT in PU nanocapsules and adding them to hybrid sol-gel pretreatments for AA2024 corrosion protection. SEM and Fourier transform infrared spectroscopy (FTIR) analyzed the generated nanocapsules morphologically. Pull-off adhesion tests were conducted on the coating systems to determine whether the presence of nanocapsules affects the coatings' adhesion and/or cohesion qualities. Electrochemical impedance spectroscopy was used to evaluate the protective qualities of sol-gel coatings containing microcapsules on a laboratory scale (EIS). Although the EIS results indicated that nanocapsules alter the coatings'

electrochemical response, the samples' visual appearance indicates that the nanocapsules improve the barrier qualities of the nanocapsule systems. When stressed by a mechanical defect, the coating system containing nanocapsules demonstrated a considerable self-healing effect, and the greater nanocapsule concentration (15 wt. percent) provided superior self-healing protection with improved anticorrosive performance. The nanocapsules did not affect the coating system's adhesion/cohesion capabilities.

MATERIALS AND METHODS
Materials
Toluene diisocyanate (≤95%, TDI), ethanol (≤98%, C_2H_5OH), chlorobenzene (≤99.8%, C_6H_5Cl), 1,2-propanediol (≤99.5%, $CH_3CH(CH_2OH)_2$), deionized water, ethylene di Amine (≤99%, EDA), Mercabutobenzimidazel (≤99%, MBI), Cyclohexane (≤99.5%, C_6H_{12}), Tetraethyl orthosilicate (≤98%, TEOS), (3. Propyl glycidyl) 97-methoxylan (% ≤, GPTMS), water pH = 2, sulfuric acid (95% ≤, H2SO4), sodium hydroxide (≤98%, NaOH) from Sigma Aldrich, gum Arabic (Merck, CAS Number: 9000-01-5), Silicon oxide (SiO_2) nanoparticles (Merck), and Komho 828 two-component epoxy resin (Raspad Shimi) were obtained and used without purification.

Synthesis of pre-polymer
TDI (6.35 gr) was added to cyclohexane (30 cc) at 80 °C and mixed with a magnetic stirrer at 200 rpm. Then, propanediol (4.5 gr) was added to the solution, and the mixing process was continued for 24 hours at 80 °C and 200 rpm until the final product formed a viscous, almost yellow liquid at the bottom of the container [1,10-12]. The sample was then placed in an oven at 80 °C for 24 hours to separate cyclohexane, and a dry solid was obtained. The obtained samples were analyzed using the FTIR test.

Synthesis of PU nanocapsules containing MBI as an anti-corrosion agent
The obtained pre-polymer (6 gr) was mixed with chlorobenzene (3 gr) at 30 °C and 300 rpm. A solution of gum Arabic (6 gr) and deionized water (54 gr) was added to the system, mixed for 30 minutes, and then MBI (0.5 gr) was added. The temperature was increased to 50 °C at a 200 rpm stirring speed. Then propanediol (6 gr) was added to the system as a chain transfer agent, and after

two hours of mixing at 250 rpm, the sample was filtered and placed in the oven for 24 hours to dry. The sample was analyzed using the FTIR test, SEM, and EDX [10-12].

Synthesis of Silane Sol-gel hybrid coating containing PU nanocapsules

The hybrid sol was synthesized by admixing silica precursors, GPTMS, TEOS, an encapsulating inhibitor, and an organic curing agent (EDTA). GPTMS and TEOS were combined at room temperature in a beaker with ethanol (12.33 cc) at a 2:1 molar ratio. The resulting two-phase solution was vigorously agitated for one hour at 240 rpm. As an acidic catalyst, water with a pH of 2 was utilized. The silane was hydrolyzed and condensed in the presence of an acid catalyst at stoichiometric and 50% sub-stoichiometric water pH 2 ethanol ratios. After hydrolysis and condensation, sol was stirred at room temperature for two hours. Two formulations, Silane-1 and Silane-2, were synthesized to apply the coatings containing 0.1 gr and 0.075 gr PU nanocapsules, respectively [10-12].

Applying self-healing and anti-corrosion coating on the Al surface

PU nanoparticles were dissolved in 2 cc of volatile solvent (chlorobenzene). Then, silane sol or two-component epoxy resin was added slowly to PU to prepare samples from 7 silane sol samples with two percent compositions of 0.1 gr and 0.075 gr. Nanoparticles and epoxy resin were used with the same number of nanoparticles, epoxy resin, and silane without nanoparticles and were dried for seven days at room temperature. Subsequently, pull-off test, SEM, and EDX operations were conducted [6,7,13].

Electrochemical analysis of the smart corrosion inhibitor nanocontainers

Electrochemical experiments were done using aqueous, air-exposed sodium chloride (5 percent NaCl) solution. Each sample was sealed with waterproof tape to avoid corrosion along the substrate's edges. A 1×1 cm region within the center of each sample was exposed to the solution during testing. A corrosion study was performed on uncoated and coated surfaces utilizing Autolab PGSTAT 30 potentiostat equipment connected to a corrosion analysis software package. At room temperature, polarization measurements were made potentiostatically using an Ag/AgCl/Cl- (0.222 V) reference electrode and a platinum counter electrode. Potentiodynamic measurements were made at a rate of 5 mV/s
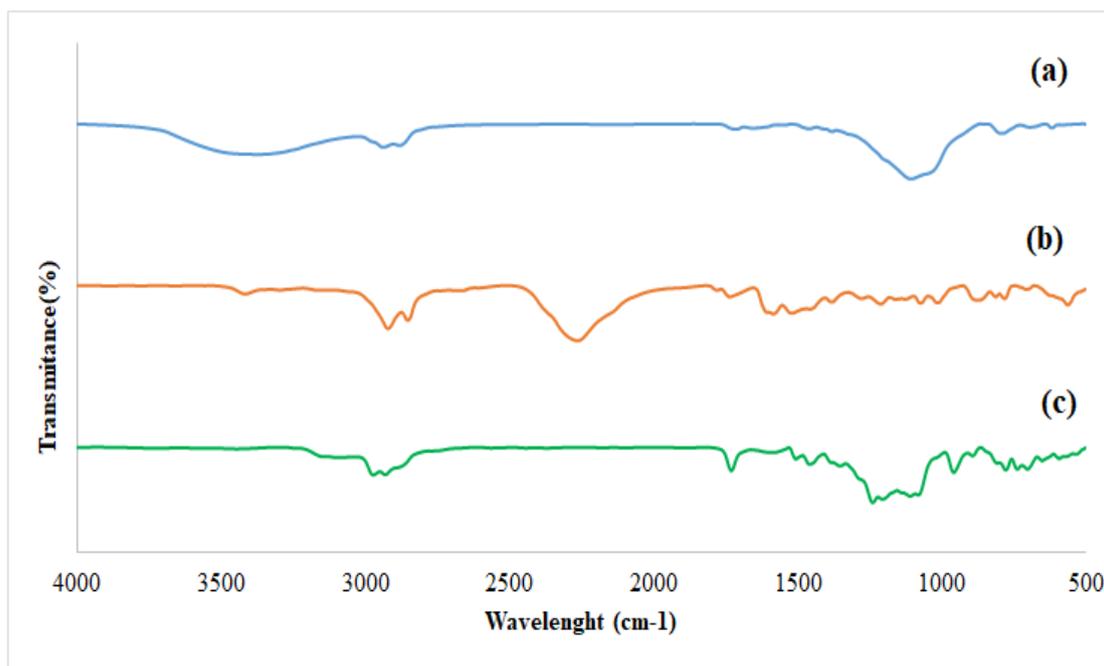

Fig. 1. FTIR spectrum of (a) MBI and (b) TDI-PD, and (c) polyurethane nanocapsules

between -2000 and 2000 mV vs. Ag/AgCl/Cl. Before the measurements, the electrodes were maintained in the working solutions for at least 30 minutes to achieve constant potential [7,13].

Characterization

A Jenavert optical microscope and a Cambridge S.360 microscope equipped with a backscattered or a secondary electron image detector operating at 10 kV and 2.85 A probe current, respectively, were used to characterize the surface morphology of the coated substrates with smart corrosion inhibitor nano containers. A UV–Vis spectrophotometer (Shimadzu UV-1650 PC) was used to determine the adsorption maxima at 242 nm [14,15]. Additionally, the average particle size was investigated using transmission electron microscopy (TEM) with a PHILIPS (Model CM120, Netherlands) at a 120 kV accelerating voltage [7,13].

Salt spray test

The corrosion resistance of self-healing coatings on steel substrates was determined using the ASTM B117 salt spray test. A series of coatings containing (a-, band c-cyclodextrin) were made on steel substrates, and the substrates' edge and backside were wrapped with water-resistant tape. The coatings were put in a salt spray chamber, and a fogging solution comprising 5% NaCl solution was administered. The salt spray chamber temperature was set to 25 °C. A total of 1000 hours were assigned to the salt spray test [7,13].

RESULTS AND DISCUSSION

The Fourier transform infrared spectroscopy (FTIR) is an efficient analytical technique for detecting functional groups and analyzing covalent bonding information. Fig. 1 shows the FTIR spectrum of MBI, pre-polymer, and PU nanocapsules containing MBI. Fig. 1-a shows MBI characteristic peaks at 3197 cm^{-1} (-N-H stretching), 2987 cm^{-1} (Ar-CH stretching), 1357 and 1267 cm^{-1} (-C-N stretching), and 601 and 653 cm^{-1} (-C-S stretching). Fig. 1-b shows peaks at 3315 cm^{-1} (secondary amine group of urethanes), 2277 cm^{-1} (an isocyanate group), and 1705 cm^{-1} (amide carbonyl group). Upon completion of the reaction, N=C=O at 2277 cm^{-1}, stretch intensity decreased, and the peaks related to the secondary amine group of urethane and amide carbonyl group shifted to higher wavelengths, 3480 and
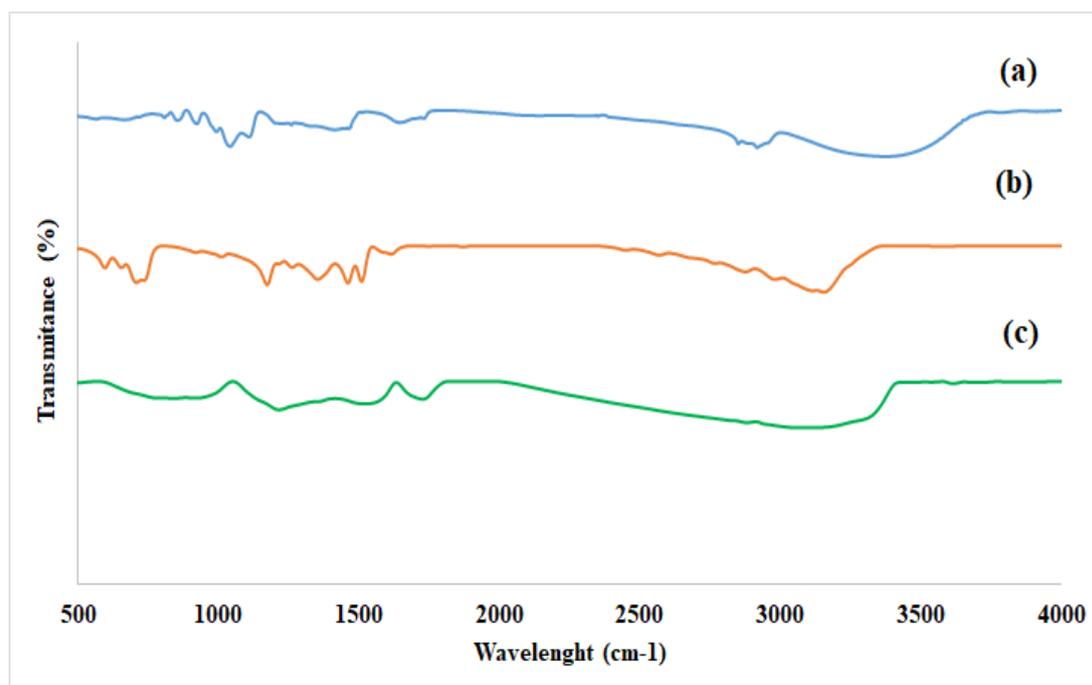

Fig. 2. FTIR spectrum of (a) SiO_2 sol, (b) SiO_2 sol -1(0.1 gr PU nanocapsules), and (c) SiO_2 sol- 2(0.0.075 gr PU nanocapsules)

1699 cm^{-1}, respectively. This suggested that a chain extender (1,4-butanediol) was employed to create a urethane linkage in the shell-wall of the microcapsule [7,13,14].

Fig. 1-c shows the PU nanocapsules containing MBI with characteristic peaks at 1705 cm^{-1} for urea linkage, 1551 cm^{-1} for carbonyl group stretching, and 3418 cm^{-1} for N–H vibration stretching from the urea linkage, which is directly associated with the carbonyl group, demonstrating the successful reaction formation of PU [13,14].

Also, the presence of MBI peaks at 1027 cm^{-1} (-C-O-C stretching), 2964 cm^{-1} (aromatic -C-H stretching), 1258 cm^{-1} (-C-N stretching), and 638 cm^{-1} (-C-S stretching) showed the presence of MBI in the PU nanocapsules. The decrease in the

isocyanate group's characteristic peak intensity at 2276 cm^{-1} suggests that virtually all –NCO groups were reacted. Silane sol-gel coating was used to apply the coating containing PU nanocapsules better. The FTIR spectrum is shown in Fig. 2. Fig. 2-a shows the peaks around 440–480 cm^{-1} (rocking transverse of SiO$_2$), strong absorption at 3500 cm^{-1} (O–H vibration), 2950 cm^{-1} (C–H stretching), 450 cm^{-1} (Si–O stretching), 670 cm^{-1} (Si–O–C stretching), 1050 cm^{-1} (Si–O–Si bending), and 1116 cm^{-1} (Si–O–Si stretching). The absorption peaks near 3342 cm^{-1} and 1630 cm^{-1} are due to hydroxyl group stretching and bending vibrations, respectively [13,14].

Figs. 2-b and 2-c show the characteristic peaks of SiO$_2$ sol, PU (2277 cm-1, N=C=O stretching), and MBI (638 cm-1 related to -C-S stretching), which

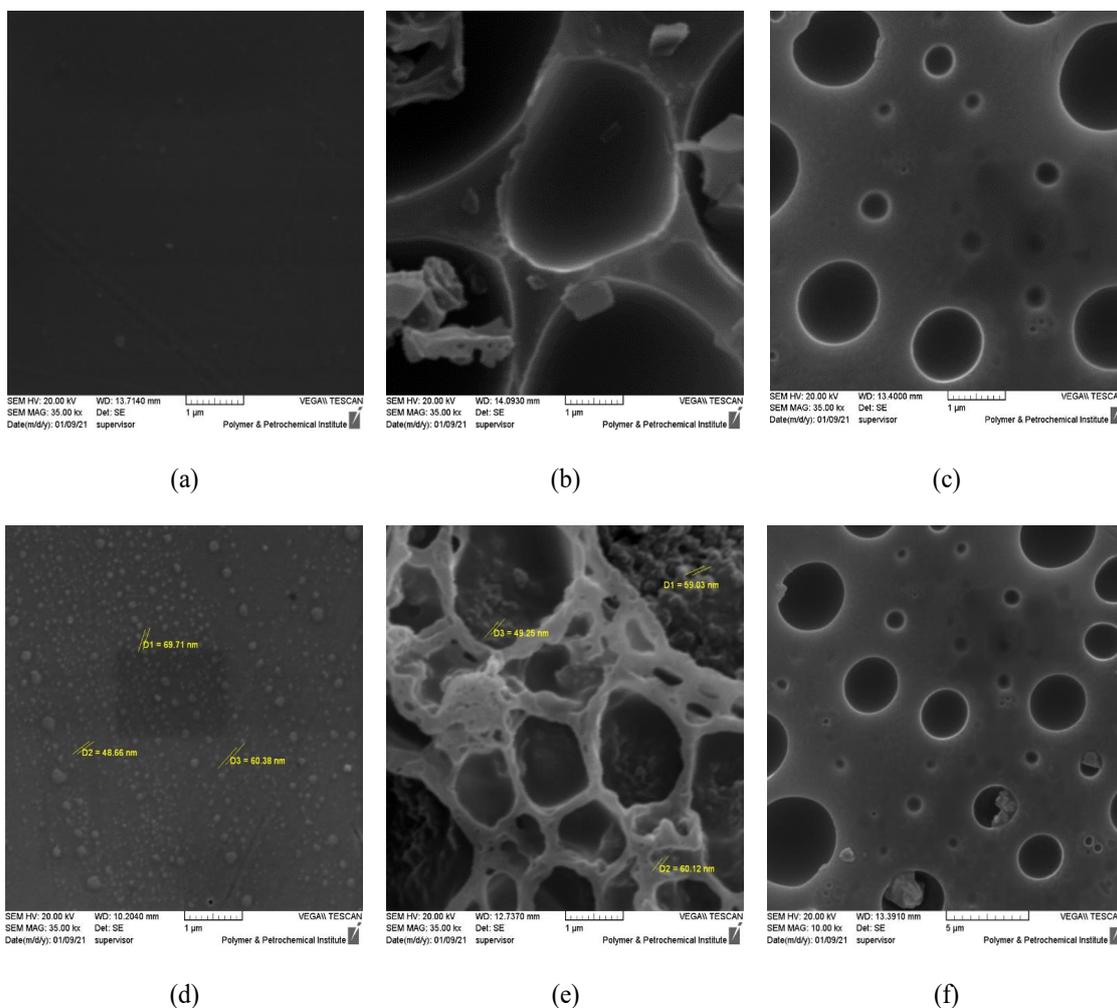(a)　　　　　　　(b)　　　　　　　(c)

(d)　　　　　　　(e)　　　　　　　(f)

Fig. 3. SEM image of pure coating of (a) Epoxy resin, (b) SiO$_2$ sol, (c) Epoxy/ SiO$_2$ sol and coating containing PU nanocapsules (0.1 gr), (d) Epoxy resin, (e) SiO$_2$ sol, and (f) Epoxy/ SiO$_2$ sol

indicate the incorporation of PU nanocapsules into SiO$_2$ hybrid sol-gel. Fig. 2-b showed that SiO$_2$ sol-1 containing a higher amount of MBI showed higher intensity for absorption at 638 cm^{-1} related to the -C-S stretching of MBI [15,17].

SEM images for the epoxy coating reveal a remarkably smooth surface film of identifiable features (Fig. 3-a). PU microcapsules, a rough topography, were observed on the smooth epoxy surface, as shown in Fig. 3 –d, and nanocapsules

were observed with good dispersion and no accumulation on the epoxy resin surface. When nanocapsules are introduced into an epoxy resin matrix, they should be uniformly scattered throughout and, more crucially, retain their geometric integrity in their dimension. Concerning SiO$_2$ sol (Fig. 3.b and e), the fracture surfaces of the sample demonstrated that the crack propagation was flat with a brittle aspect. SEM fracture surface images of the epoxy coating and epoxy/SiO$_2$
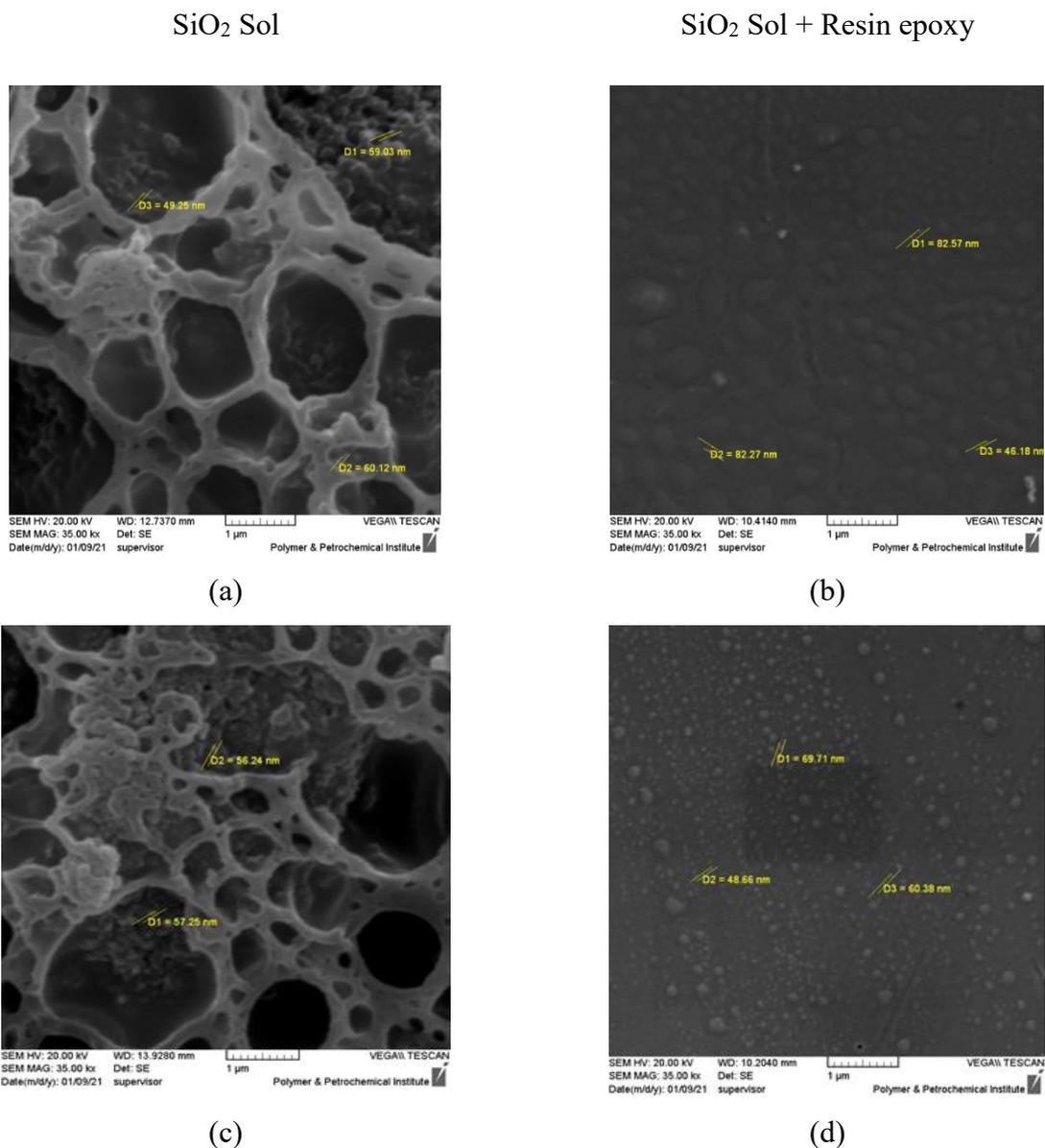
SiO$_2$ Sol

SiO$_2$ Sol + Resin epoxy

(a)

(b)

(c)

(d)

Fig. 4. SEM image of SiO$_2$ Sol and Resin epoxy containing (a, b) 0.1 g PU nanocapsules and (c, d) 0.0.75 g PU nanocapsules.

hybrid coating (Fig. 3c and 3f) revealed a two-phase system. Epoxy coatings have a single-phase fracture surface morphology, whereas epoxy/SiO_2 hybrid coatings have a good double-phase structure. According to Fig. 3c, the second phase particles arise in the epoxy/SiO_2 hybrid coating and are homogeneously spread in the epoxy matrix.

Fig. 4 shows higher amounts of PU nanocapsules in the coating surfaces and larger nanocapsules. The nanocapsules' size is about 60 nm for SiO_2 sol containing 0.1 gr PU nanocapsules and about 56 nm when 0.075 gr PU nanocapsules were incorporated into the coating. Figs. 4-b and 4-d show an excellent PU nanocapsule distribution due to the smooth surface of the epoxy resin and better compatibility of urethane nanocapsules with an epoxy substrate. EDX test results confirm the uniform presence of urethane nanocapsules on the coating surface (Figs. 5 and 6).

Pull off test

Pull-off testing determined the adhesion strengths of the produced self-healing coatings.

According to Table 1, adding nanocapsules lowered the net coating's adhesion strength. Increasing the concentration of PU nanocapsules resulted in a more significant reduction, which may be attributed to the agglomeration of PU nanocapsules and their high surface area, which led to more resin adsorption. This is because of various imperfections in the PU nanocapsules at the interface, which result in low adhesion pots where they come into touch with the substrate. Thus, by increasing the percentage of PU nanocapsules in the coating, the adhesion of the coating is reduced due to agglomeration.

Salt Spray Test

Comparing the results of the obtained coatings (with and without PU nanocapsules) showed that the best and optimum self-healing coating sample contains 0.1 gr PU nanocapsules (Fig. 7). After 240 hours of immersion in the presence of 5 wt% of sodium chloride solution, coatings containing 0.1 gr PU nanocapsules showed the best level of self-healing capability. Without PU nanocapsules, SiO_2
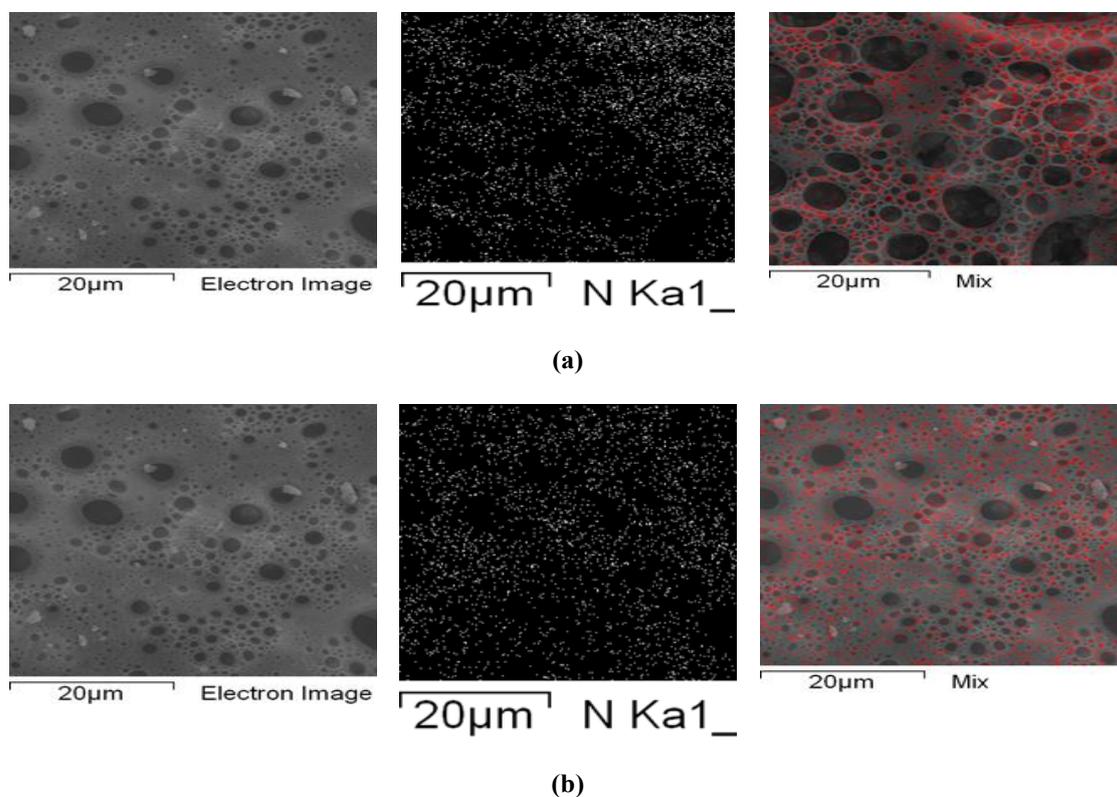

(a)

(b)

Fig. 5. EDX images of SiO_2 sol containing PU nanocapsules (a) 0.1 g of PU nanocapsules, and (b) 0.075 g of PU nanocapsules
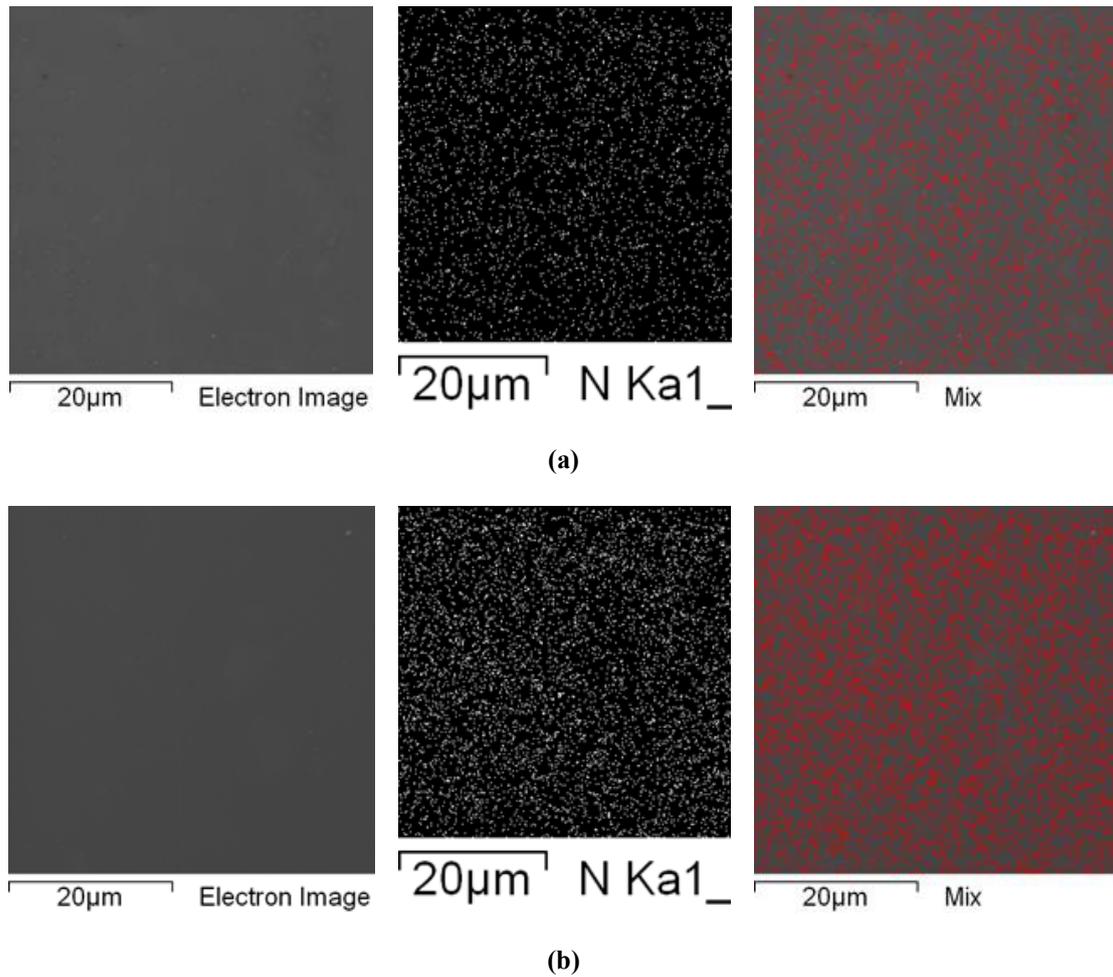
(a)

(b)

Fig. 6. EDX images of epoxy coating containing PU nanocapsules (a) 0.1 g of PU nanocapsules, and (b) 0.075 g of PU nanocapsules

Table 1. Pull-off test on coatings

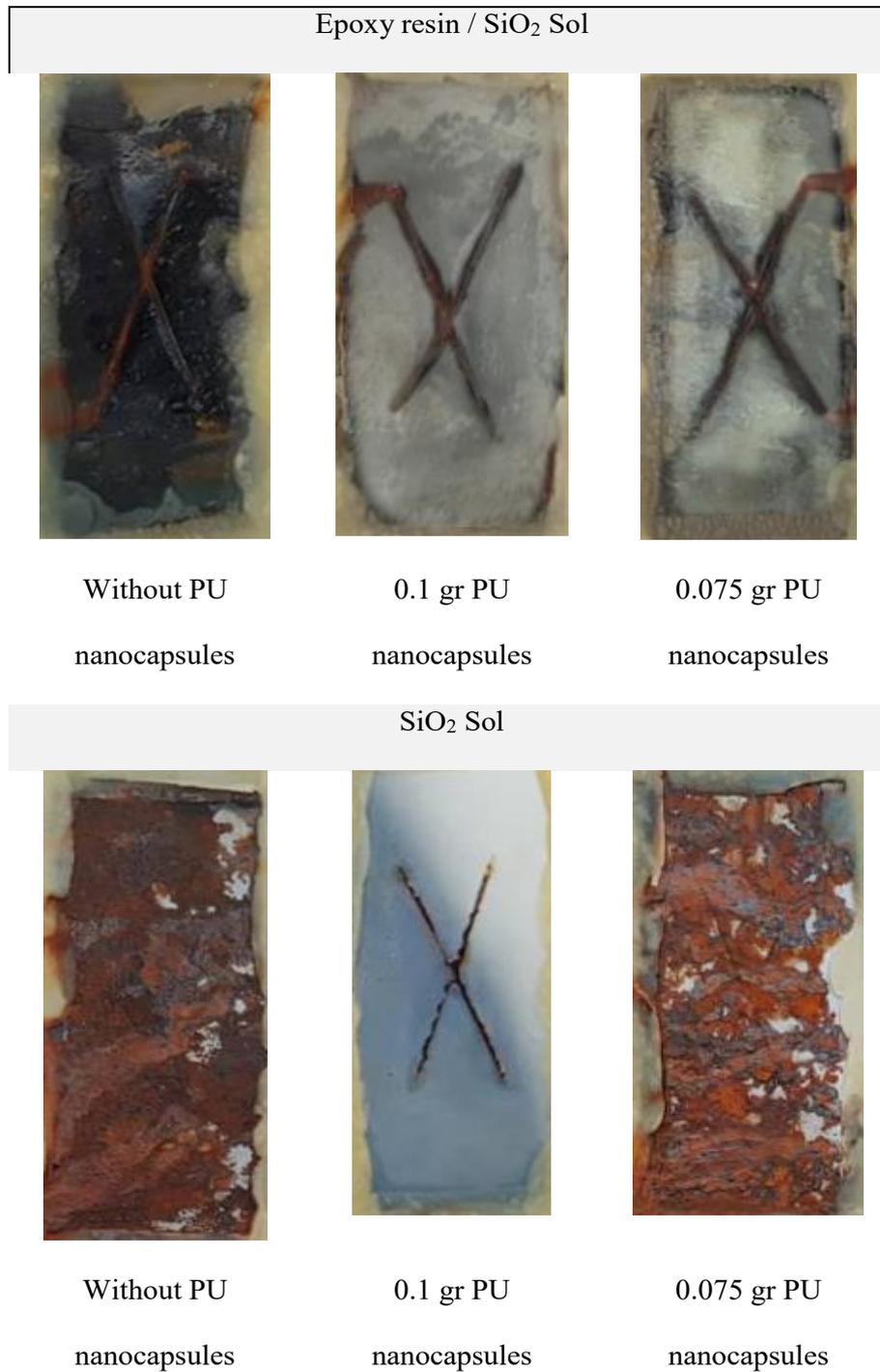| Sample	PU nanocapsules (g)	MPa
SiO_2 sol	0	Fail
SiO_2 sol-1	0.1	0.70
SiO_2 sol-2	0.075	0.95
Epoxy resin	0	1.24
Epoxy resin 1	0.1	0.85
Epoxy resin 2	0.075	1.4
SiO_2 sol/ Epoxy resin	0	1.31
SiO_2 sol/ Epoxy resin-1	0.1	1.35
SiO_2 sol/ Epoxy resin-2	0.075	1.7

Fig. 8. Frequency impedance diagram (Bode) for samples of (a) resin epoxy, (b) resin epoxy with 0.1 gr PU nanocapsules, and (c) resin epoxy with 0.075 gr PU nanocapsules in 0 hours (30 minutes).

sol and Epoxy resin/SiO_2 sol entirely corroded and formed significant rust, most prominently within the groove of the scribed regions [17].

For samples with 0.1 gr PU nanocapsules (SiO_2 Sol and Epoxy resin /SiO_2 Sol), after 240 hours of exposure to salt spray, there was no visible corrosion, attributed to the presence of PU nanocapsules carrying MBI, which operate as
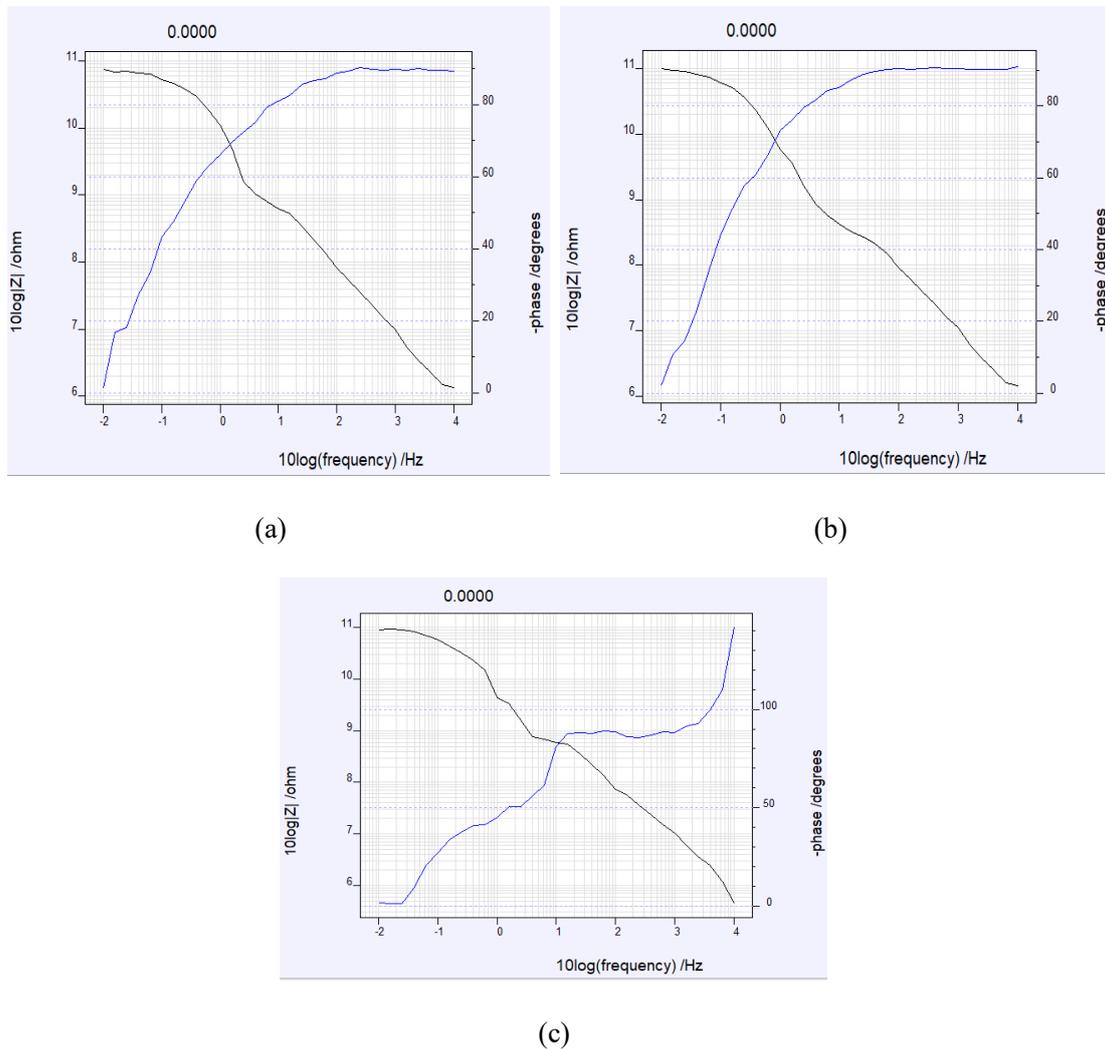
(a)

(b)

(c)

Fig. 9. Impedance diagram in terms of frequency (Bode) for samples (a) resin epoxy, (b) resin epoxy with 0.1 gr PU nanocapsules, and (c) resin epoxy with 0.075 gr PU nanocapsules in 5 hours.

a corrosion inhibitor and so can be employed for long-term corrosion protection. Regarding the samples with 0.075 gr PU nanocapsules, SiO_2 sol coatings showed complete corrosion due to holes in the morphology of the coating (Fig. 4), which caused the corrosive fluid to penetrate the coating and destroy the sample. Therefore, protection against corrosion requires higher amounts of PU nanocapsules [17].

Electrochemical impedance spectroscopy (EIS) test

Electrochemical impedance spectroscopy is a common method for investigating and assessing self-healing protective coatings for metals to evaluate corrosion-related physiochemical processes on coated surfaces. One of the most popular methods for EIS results is the Bode diagram, which is based on the logarithm of the frequency versus the amount of impedance absorption (| Z = Z0) and phase shift. Bode diagrams are mainly used for coated metal surfaces with defective coatings to investigate the self-healing phenomenon. The impedance at low frequency suddenly decreases by creating artificial cracks in the coating surface due to the breakdown of the oxide film and the beginning of the corrosion process. For example, the Bode diagram for tracking the self-healing properties of coatings containing corrosion-
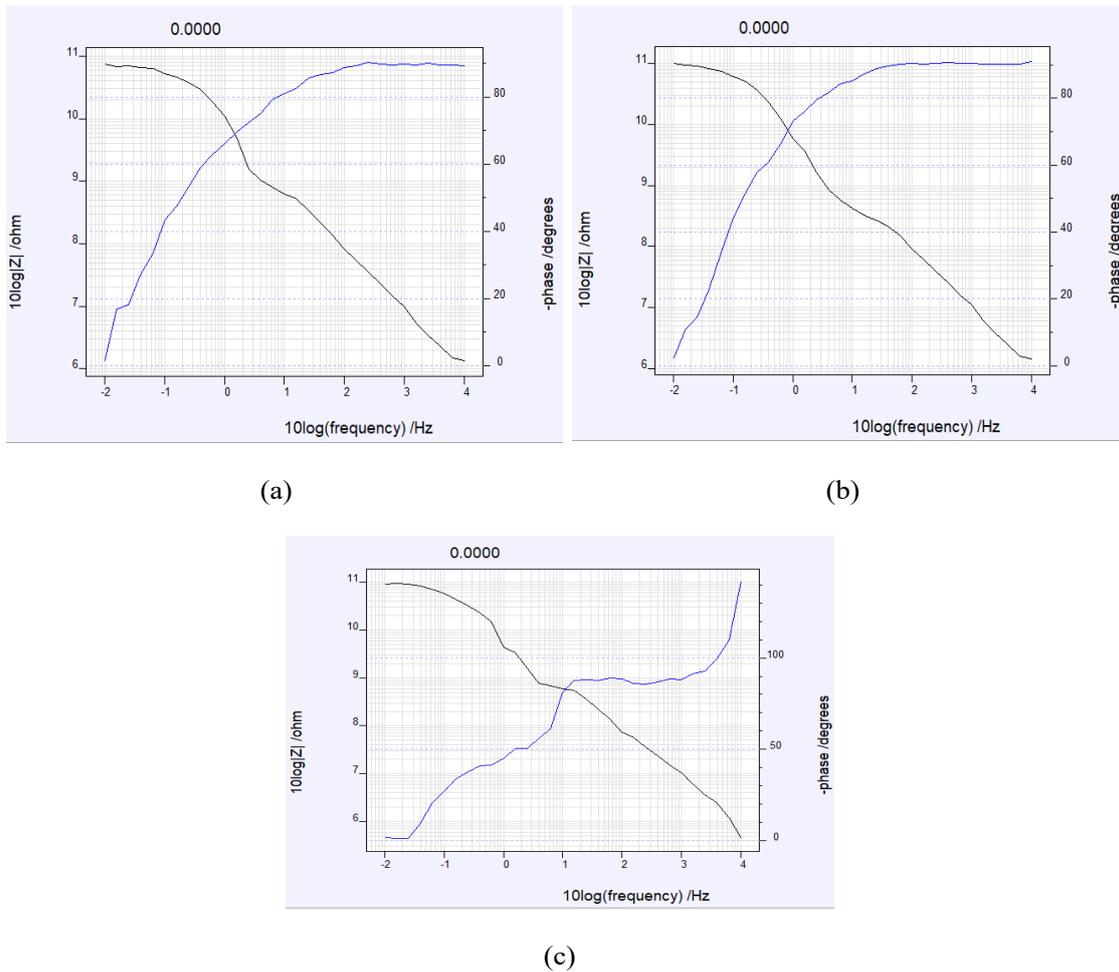
(a)

(b)

(c)

Fig. 10. Frequency impedance diagram (Bode) for samples (a) resin epoxy, (b) resin epoxy with 0.1 gr PU nanocapsules, and (c) resin epoxy with 0.075 gr PU nanocapsules.

inhibiting nanocapsules on the aluminum surface is shown in Figs. 8 to 10. MBI-based nanocapsules were used in the coatings as corrosion inhibitors [15-18].

The protected alloys exhibit extremely resistive characteristics with extremely low current density values, a characteristic of nonconductive materials. A drop in the corrosion current density is found in samples coated with PU nanocapsules, which is critical for the alloy's corrosion protection. The protective coating with encapsulated MBI is exceptionally effective at passivating and protecting the alloy surfaces, as seen by the extremely low current density values observed in the polarization curves. Tafel extrapolations indicate that the nanocapsule-based coating resulted in a positive shift in the corrosion potential

compared to the bare sample. The polarization curves of corrosion of the inhibitor-containing coatings exhibit well-defined passivation areas indicating inhibitor activity of the encapsulated MBI retain their inhibitory activity.

The impedance of the bare sample decreases, indicating that the coating is beginning to delaminate, which is more likely within the scribed area due to a corrosion attack at the coating/substrate interface [17,18].

CONCLUSION

In the present research, PU nanocapsules containing MBI inhibitor was mixed withepoxy resin with different compositions (0 and 0.1 gr and 0.75 gr)and coated on the surface of steel plates was investigated.

The synthesized samples were analyzed using Fourier transform infrared spectroscopy and SEM-EDX, Pull-off, salt spray, and electrochemical impedance spectroscopy tests. The results showed the successful synthesis of silane sol and nanocapsules containing polyurethane inhibitors. SEM results show that the size of the nanocapsules is about 60 nm for SiO_2 sol containing 0.1 gr PU nanocapsules and about 56 nm when 0.075 gr PU nanocapsules were incorporated into the coating. They also showed an excellent distribution due to the smooth surface of the containing epoxy resin and better compatibility of urethane nanocapsules with an epoxy substrate. EDX test results prove urethane nanocapsules' uniform presence on the coating surface. Pull-off test results confirmed that increasing the concentration of PU nanocapsules in the matrix attributed to the agglomeration of PU nanocapsules and their high surface area led to more resin adsorption. Comparing the salt spray test results of the obtained coatings proves that the optimum and best self-healing coating sample contains 0.1 gr PU nanocapsules and offers the best self-healing capability. Electrochemical impedance spectroscopy confirmed the improvement of anti-corrosion properties in epoxy coating systems. Accordingly, the polyurethane microcapsules could extend the service life of the polyurethane coatings and offer promising self-healing results.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

REFERENCES

1. Xiang G, Tu J, Xu H, Ji J, Liang L, Li H, et al. Preparation and Self-Healing Application of Isocyanate Prepolymer Microcapsules. Coatings. 2022;12(2):166.
2. Amiri S, Rahimi A. Hybrid nanocomposite coating by sol–gel method: a review. Iranian Polymer Journal. 2016;25(6):559-577.
3. Amiri S, Amiri S. Cyclodextrins: Wiley; 2017 2017/09.
4. Zhang F, Ju P, Pan M, Zhang D, Huang Y, Li G, et al. Self-healing mechanisms in smart protective coatings: A review. Corros Sci. 2018;144:74-88.
5. Ismail NA, Khan A, Fayyad E, Kahraman R, Abdullah AM, Shakoor RA. Self-Healing Performance of Smart Polymeric Coatings Modified with Tung Oil and Linalyl Acetate. Polymers. 2021;13(10):1609.
6. Amiri S, Amiri S. Inhibitors-loaded nanocontainers for self-healing coatings. Corrosion Protection at the Nanoscale: Elsevier; 2020. p. 379-402.
7. Amiri S. Containers with Anti-Corrosion Agents for Metal Protection Paints. Micro- and Nano-containers for Smart Applications: Springer Nature Singapore; 2022. p. 213-241.
8. Santamaria-Echart A, Fernandes I, Barreiro F, Corcuera MA, Eceiza A. Advances in Waterborne Polyurethane and Polyurethane-Urea Dispersions and Their Eco-friendly Derivatives: A Review. Polymers. 2021;13(3):409.
9. Xu H, Tu J, Xiang G, Zhang Y, Guo X. A Thermosetting Polyurethane with Excellent Self-Healing Properties and Stability for Metal Surface Coating. Macromolecular Chemistry and Physics. 2020;221(20):2000273.
10. Li M, Ding H, Yang X, Xu L, Xia J, Li S. Preparation and Properties of Self-Healing Polyurethane Elastomer Derived from Tung-Oil-Based Polyphenol. ACS Omega. 2019;5(1):529-536.
11. Javidi M, Fathi Fathabadi H, Jenabali Jahromi SA, Khorram M. Investigating the interfacial synthesis of polyurethane microcapsules and optimization of the process using response surface method. Materials Research Express. 2019;6(10):105302.
12. Alizadegan F, Mirabedini SM, Pazokifard S, Goharshenas Moghadam S, Farnood R. Improving self-healing performance of polyurethane coatings using PU microcapsules containing bulky-IPDI-BA and nano-clay. Progress in Organic Coatings. 2018;123:350-361.
13. Rahimi A, Amiri S. Self-healing anticorrosion coating containing 2-mercaptobenzothiazole and 2-mercaptobenzimidazole nanocapsules. Journal of Polymer Research. 2016;23(4).
14. Koh E, Baek S-Y, Kim N-K, Lee S, Shin J, Kim Y-W. Microencapsulation of the triazole derivative for self-healing anticorrosion coatings. New Journal of Chemistry. 2014;38(9):4409.
15. Amiri S, Rahimi A. Anticorrosion behavior of cyclodextrins/inhibitor nanocapsule-based self-healing coatings. Journal of Coatings Technology and Research. 2016;13(6):1095-1102.
16. Cotting F, Koebsch A, Aoki IV. Epoxy Self-Healing Coating by Encapsulated Epoxy Ester Resin in Poly (Urea-Formaldehyde-Melamine) Microcapsules. Frontiers in Materials. 2019;6.
17. Fan W, Li W, Zhang Y, Wang W, Zhang X, Song L, et al. Cooperative self-healing performance of shape memory polyurethane and Alodine-containing microcapsules. RSC Adv. 2017;7(74):46778-46787.
18. Yang H, Mo Q, Li W, Gu F. Preparation and Properties of Self-Healing and Self-Lubricating Epoxy Coatings with Polyurethane Microcapsules Containing Bifunctional Linseed Oil. Polymers. 2019;11(10):1578.