Self-healing and corrosion performance of polyurethane coating containing polyurethane microcapsules

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Abstract

In this study, the self-healing behavior of the polyurethane coating containing polyurethane microcapsules was investigated. Microcapsules, with the average size of 99 μm and shell thickness of 11 μm, were successfully synthesized via the interfacial polymerization technique and were incorporated into the polyurethane coating matrix. The electrochemical impedance spectroscopy and scanning electron microscope were employed to investigate the healing performance and corrosion behavior of the coatings on the carbon steel substrate. The recorded results revealed that artificial scratches were successfully healed and the coating containing 20 wt% microcapsules exhibited the best healing performance (85% healing efficiency) among all the prepared coatings. The self-healing ability of the coatings were verified via scanning electron microscope. After 24 hours, the healing efficiency attained a reasonable value of 68% during exposure to test solution. It was found that corrosion resistance and coating adhesion were significantly improved by incorporating the microcapsules into the coating.

Introduction

Protecting metallic substrates against corrosion has become a hot topic in various industries. Some environments would lead to the corrosion of metals and alloys, followed by an inevitable failure and rupture during service life. Polymers and composites have been widely used for diverse applications, especially as a barrier coating on different metallic substrates in front of harsh environments. Painting is a common and efficient method to protect metallic surfaces. However, the diffusion of corrosive species into protective coatings can result in corrosion of metallic substrate followed by formation of micro-cracks through the coating. The presence of micro-cracks leads to the failure of the coatings and deterioration of the substrates.

For the last decades, the application of smart coatings with self-healing ability has undoubtedly increased a lot of attention to recover minor damages automatically. Self-healing coatings can improve the operational capability of the system in addition to extending service life by saving time, cost, and equipment downtime. Moreover, these systems provide an inherent ability to detect and prevent chemical changes associated with corrosion autonomously. Consequently, they reduce the need for local inspection and repairing corroded area.[1] Self-healing systems can be classified into four main groups, including capsule embedment,[2, 3] hollow fiber embedment,[4] microvascular system,[5, 6] and intrinsic base.[5] Each system has some potential limitations and challenges so that their limitations affect the carrier thickness. According to literature, a thickness of more than 100 μm is undesirable.[7] Therefore, microencapsulation is one of the most commonly used techniques in self-healing applications. In this system, microcapsules containing healing agents in a trapped state are dispersed through the passive coating matrix. The collision of micro-cracks associated with the degradation and mechanical damage of the protective coating (containing micro/nano capsules) results in the release of the healing agent followed by a reaction with the passive matrix to repair the defective coating. The healing agent would react with oxygen,[8] moisture,[9] sunlight,[10] or other crosslinkers[11] to develop a new layer. Besides, using

microcapsules containing suitable healing material could considerably enhance the corrosion performance of protective coatings.[12]

The first encapsulation technique was introduced by White et al.[13] Since then, lots of investigation have been made to improve healing techniques in polymeric coatings. Accordingly, different types of capsules such as polyurethane,[14–16] phenol-formaldehyde resin,[17, 18] and urea-formaldehyde resin [12, 19] were prepared of which urea-formaldehyde microcapsules have been extensively utilized for polymer composite systems, despite the challenges and limitations of preparation procedure.[20] Furthermore, polyurethane microcapsules have been widely used for self-healing composites[14, 16, 21] because they provide good compatibility with various materials and exhibit excellent adhesion to many substances. Moreover, the polyurethane shell is controllable because of broad possible variations in synthesizing polyurethane.

The healing ability of a polymer matrix depends on various factors, including chemical composition, viscosity, healing agent reactivity, and relative amount of healing agent to matrix.[7] Furthermore, the compatibility of the healing agent with matrix material can provide a superior achievement in recovery of original properties of matrix material.

A variety of techniques have been employed to synthesize microcapsules of which interfacial polymerization has been at the center of interest because of its facile preparation procedure.[7, 16, 22] Therefore, this technique is frequently used for fast synthesis of polyurethane microcapsules with reasonable synthesis conditions;[23] it involves the reaction of two or more monomers at interface of two immiscible phases which are carefully emulsified to form microscopic droplets in the medium.

Wide-ranging materials have been encapsulated as healing agents using different methods like polyurethane,[16] epoxy resin,[3] amines,[24] inhibitors,[25] linseed oil,[26] Tung oil,[27] and Hexamethylene diisocyanate (HDI)[28] for polymeric coatings. However, the corrosion resistance of the new layers formed by oil films and alkyds is not satisfying.[29] Among these materials, polyurethane with good mechanical property, high chemical and corrosion resistance in addition to reasonable cost represents an excellent candidate for self-healing applications.[16, 30] Moreover, the high thermal decomposition temperature of the polyurethane resin could make microcapsules with a superior thermal stability. These features ensure that polyurethane can act efficiently as both core and shell material to repair minor damages without additional heat or catalyst. It should be noted that polyurethane microcapsules could provide good compatibility with polyurethane coating systems and great adhesion to the polyurethane coating matrix. The healing process will occur due to the polymerization process between the polyurethane resin (released from the ruptured microcapsules) and the hardener, based on the reaction of the hydroxyl group (-OH) and isocyanate group (-OCN). However, the self-healing ability and the efficiency of the microcapsules should be improved.

In our previous work,[31] interfacial polymerization was successfully employed to synthesize the

re and shell material. The Response surface

methodology (RSM)-based Design of experiments technique (DOE) was employed to optimize the effect of parameters like agitation speed, homogenization time, and the amount of hardener as the most important controlling parameters on the size, shell thickness, efficiency, and core content of the microcapsule. A model was proposed to estimate the optimized conditions for the synthesized microcapsules. To the best of our knowledge, using the polyurethane resin as a healing substance within the polyurethane coatings has not been widely investigated thus far. There is not enough relevant publication concentrated on the effect of polyurethane resin, as the healing agent, on anticorrosive characteristic of polyurethane coatings. In the present study, the obtained microcapsules under the optimized condition were added to the polyurethane resin as a barrier coating on carbon steel substrate. This work aimed to investigate the healing ability of the polyurethane coatings containing polyurethane microcapsules. Hence, the smart coatings were prepared by incorporating different weights of the microcapsules into the polyurethane coatings. The self-healing ability and corrosion resistance of coatings along with artificial cracks in a 3.5% NaCl corrosive solution were investigated via electrochemical impedance spectroscopy (EIS). To obtain the size and morphology of the capsules, and to evaluate their self-healing performance, scanning electron microscope (SEM) was utilized.

Experimental

Materials

Aliphatic polyurethane resin and its hardener (based on Hexamethylene diisocyanate) were purchased from a local resin provider. The polyurethane resin was used as the investigated material for the coating matrix, the healing agent and the shell monomer. The polyurethane resin's hardener was used as the curing agent for polyurethane monomer to develop the shell. Tween 80 and Arabic gum (Korean Daejung Company) were employed as emulsifiers.

Preparation of Microcapsules

The polyurethane microcapsules were synthesized via interfacial polymerization as below; 0.80 g Arabic gum, 0.60 g Tween 80, and 40 ml deionized water were emulsified mechanically at 50 ºC for 1 hour to achieve a uniform and stable emulsion. To adjust the pH at 11, NaOH solution (diluted with deionized water) was added dropwise to form serious microcapsules. After that, the polyurethane resin was dissolved in 20 ml Acetone (at room temperature) as an oil phase and then was slowly spilled into the aqueous phase under mechanical stirring at speed of 2155 rpm for 26 minutes to reach the temperature of 60 ºC. Finally, the hardener was added dropwise into the mixture and the stirring rate was kept at the mentioned temperature for 2 hours. It should be noted that acetone, as a volatile material, leaves the emulsion before temperature reaches 60 ºC. In fact acetone was utilized to incorporate the resin to micelles in the aqueous solution. The schematic of the fabrication procedure can be illustrated as shown in Fig. 1. The microcapsules from colloidal solution were recovered by filtration, rinsed with deionized water, and finally dried in air for 24 hours before going to vacuum oven at 40 ºC for 24 hours.[31]

SEM Investigation

Morphology, size distribution, and shell thickness of the prepared microcapsules were observed and characterized by Scanning Electron Microscopy (SEM-Cambridge Stereoscan S360). The surface morphology of the coatings at artificial cracks was also verified by SEM photomicrographs to investigate the healing process.

Coatings Application

The synthesized microcapsules were dispersed into polyurethane resin, blended with isocyanate hardener with weight ratio of 4:1 at room temperature. The embedded-microcapsules polyurethane resin was homogenized by a mechanical mixer. After that, the resin was coated uniformly on the surface of carbon steel plates (2 cm × 2 cm) via a film applicator to reach dry film thickness of 250 µm. For the sake of the optimum self-healing behavior of the coatings, a series of coatings were prepared using different weight percentages of microcapsules as shown in Table 1. For a better comparison, a neat polyurethane coating (with and without scratch) and a bare carbon steel sample were equally considered.

Table 1
Prepared and coded samples.

Samples' Code	Polyurethane Coating
SC-0%	Scratched coating with 0 wt% microcapsules
SC-10%	Scratched coating with 10 wt% microcapsules
SC-15%	Scratched coating with 15 wt% microcapsules
SC-20%	Scratched coating with 20 wt% microcapsules
SC-25%	Scratched coating with 25 wt% microcapsules
SC-30%	Scratched coating with 30 wt% microcapsules
UC-0	Unscratched coating with 0 wt% microcapsules
UC-20%	Unscratched coating with 20% microcapsules
Bare Steel	Bare Carbon Steel

Evaluation of Self-healing Behavior of the Coatings and Corrosion Performance

Electrochemical impedance spectroscopy (EIS) was employed to investigate the self-healing behavior and corrosion performance of coatings. After applying the coatings, the samples were left in atmosphere for 3 days to allow curing process to be completed. Furthermore, 2 cm crossed-scratched lines (X-cut) were created artificially on the coated samples using a razor blade. The scratches had the size of 250 µm depth and \tilde 50 µm width. The blade reached the metallic substrate to let the corrosive media contact

with the surface, and then the samples were laid in atmosphere to enable the healing process to occur. The healing performance and corrosion behavior of the coatings were evaluated via EIS investigations in 3.5 wt% NaCl aqueous solution (the test solution) at 27°C. The area of the coatings investigated was limited to 1 cm^2 using a flat cell as shown in Fig. 2. In this cell, the investigated sample, platinum, and Saturated Ag/AgCl electrodes were utilized as working electrode, counter, and reference electrodes; respectively. The electrochemical measurements were performed by Metrohm Autolab Model µlab3 potentiostat. Moreover, all the measurements were repeated three times to ensure reproducibility, and the average data were reported. EIS tests were performed in a frequency range of 10^5 to 10^{-2} Hz and an amplitude sinusoidal AC potential of ±10 mV. The resulted data were analyzed by employing ZView Software from Scribner Associates.

Adhesion Test

To evaluate coating adhesion to the substrate, adhesion test was accomplished based on ASTM D3359 test method A. Four samples, including coatings containing 10, 20, 30 wt% microcapsules, and a neat coating without microcapsules, were prepared. In this test, a pressure-sensitive adhesive tape was used to check the coatings' adhesion and strength. Initially, a 2 cm long X-cut by angle of 30° was made to reach the metallic substrate by a razor blade on the free-contamination coating. Then, the adhesive tape was stuck on the desired surface and separated from the surface again. The degree of adhesion of the coatings to the surface was qualitatively evaluated on the scale of 0A to 5A according to ASTM D3359 method A scale.

Results And Discussion

Characterization of the Synthesized Microcapsules

The SEM photomicrographs of the microcapsules obtained are demonstrated in Fig. 3. The average diameter of the microcapsules was measured to be ~ 99 µm and the shell thickness was ~ 11 µm. It is consistent with the fact that the capsules size should be in the range of 60–150 µm for self-healing applications.[2, 3, 32] Moreover, the larger size of microcapsules provide more amounts of healing agents in the damaged area; therefore a damaged coating could be healed effectively with larger capsules. [2]As a result, the synthesized microcapsules are suitable for self-healing applications. On the other hand, it can be seen that the microcapsules are spherical and the outer surface is almost rough that helps good adhesion to the matrix. Furthermore, the spherical shape of the microcapsules ascertains the storage of healing agent. In order to assure the presence of healing agent inside the capsules, they were crushed and observation with SEM showed that they are filled with healing agent as can be seen in Fig. 3b. Then, the crushed microcapsules were washed with acetone to collect the core material, so the inner face and the shell of the microcapsules can clearly be seen in Fig. 3C.

Self-healing Performance of the Coatings

The healing mechanism of microcapsules in the coating matrix to protect metallic substrates is schematically illustrated in Fig. 4. The micro-cracks associated with external forces rip the microcapsules and release the healing agent in cracked area; the released healing agent reacts with surrounding coating and heals the defected zone. This process can lead to the original property restitution of the cracked area in the polymer coating as long as the released healing agent fills the crack, although it could not entirely cover the damaged area. Consequently, the newly formed layer prevents the diffusion of the corrosive species through the coating and inhibits the corrosion of the substrate. The release of polyurethane resin, as core material and the healing agent from the investigated microcapsules can result in two polymerization processes. The first one is the reaction of hydroxyl groups of polyurethane in the core and isocyanate-based hardener in the matrix. The second one represents the reaction of polyurethane molecules. The amount of hardener in the coating should be exceeded the stoichiometric one, to assure the curing process of the released polyurethane resin from the microcapsules. In this manner, the reaction of the released polyurethane resin with available extra curing agent in the polyurethane coating matrix could result in curing the resin in the defective area, so healing is achieved. The curing reaction of the isocyanate monomers in the ambient condition takes place in a long time (in a free-catalyst system).[21, 33] If the isocyanate monomers could react with the atmospheric moisture, the new products prevent the diffusion of moisture and ions through the coatings. Consequently, the isocyanate monomers remain intact beneath the formed layer for a much longer time in practice, until the atmospheric moisture could diffuse to reach the remaining isocyanate.[7] In a free-catalyst system, the low-rate reactions cause a low-physical/chemical quality layer to form in the damaged zone.[21] The significant advantage of such a system is that the coating matrix and the microcapsules (core and shell material) have the same composition, which provides a facile and economical procedure for self-healing coatings applications.

The Effect of Microcapsule Concentration on Healing Process

EIS test has been widely used to assess the self-healing performance and corrosion behavior of the coatings.[34] EIS is an efficient method so that coating performance can be evaluated before appearance of any sign of rusting and blistering on coating samples. The presence of ions affects the coating resistivity; thus this parameter can be employed to evaluate the healing and corrosion performance of the coatings.

The practical efficiency of the healing process critically depends on the sufficient amount of healing agent that can be adequately provided in the damaged region. It was reported that the best healing performance in the microcapsule-base self-healing coatings was observed for the microcapsules concentration of more than 10 wt%.[2, 3, 35] Therefore, to investigate the potential effect of the microcapsule concentration on healing performance, the polyurethane coatings containing 10, 15, 20, 25, and 30 wt% polyurethane microcapsules were carefully prepared and EIS measurements were implemented in the test solution. Furthermore, a sample of polyurethane coating without any microcapsules (with and without scratches thereon) was prepared to accurately determine the possible

es of the coatings.

The resulted Bode magnitude, Bode phase diagrams and Nyquist plots from electrochemical investigations of the samples are illustrated in Figs. 5 and 6 and the extracted electrochemical data are presented in Tables 2 and 3. According to Fig. 5a, Bode plots show that the total impedance (|Z|) was increased by increasing the amount of microcapsules up to 20 wt%. This can be explained by the fact that the amount of healing agent in the damaged region is not sufficient when the concentration of microcapsules is inadequate and too low. Besides, increase in the concentration of microcapsules from 20 to 30 wt% reduces the values of total impedance. The observed decrease in impedance could be attributed to the increase in coating porosity which let the corrosive species diffuse through the coating.[3] In other words, the increase in the concentration of the microcapsules up to 20 wt% resulted in a continuous improvement in the healing performance while a decline was then observed.

Table 2
The resulted electrochemical data after curve fitting the impedance results for carbon steel samples coated with polyurethane resin containing different concentrations of polyurethane microcapsules in 3.5% NaCl electrolyte.

Samples		CPE Coat			CPE Double Layer		
		Q_C			Q_{dl}		
	R_{po} ($k\Omega.cm^2$)	$Y_0 \times 10^{-6}$ ($S^n.\Omega^{-1}.cm^{-2}$)	n	R_{ct} ($k\Omega.cm^2$)	$Y_0 \times 10^{-6}$ ($S^n.\Omega^{-1}.cm^{-2}$)	n	Efficiency η (%)
Bare Steel	-	-	-	1.2	4543	0.72	-
SC-0%	4.0	2721	0.72	0.9	4232	0.60	-
SC-10%	11.4	218	0.97	1.7	321	0.75	64
SC-15%	15.5	324	0.94	2.8	388	0.77	74
SC-20%	27.4	252	0.91	4.5	298	0.72	85
SC-25%	7.3	2546	0.72	0.8	2871	0.58	45
SC-30%	3.3	3872	0.70	0.1	4102	0.59	-

Table 3
The resulted electrochemical data after curve fitting the impedance results for the carbon steel samples coated with polyurethane resin containing 20 wt% polyurethane microcapsules and the neat coating without any scratches in 3.5% NaCl electrolyte.

		CPE Coat	
		Q_c	
Samples	R_{po} ($k\Omega.cm^2$)	$Y_0 \times 10^{-6}$ ($S^n.\Omega^{-1}.cm^{-2}$)	n
UC-0%	110500	4.8	0.89
UC-20%	1668	11.2	0.91

Based on what has been reported, the EIS data of the polymer-coated metals could be interpreted via two-time constants equivalent circuit encompassing R_pQ_c of the pore resistance, as well as coating capacitance, and $R_{ct}Q_{dl}$ for surface corrosion effects and double-layer capacitance.[35, 36] According to the EIS plots, two-time constants were observed. Thus, the data obtained were fitted with the equivalent circuit showed in Fig. 7 and the resulted data are tabulated in Table 2. Due to intrinsic inhomogeneity, a constant phase element (CPE, showed by Q) could be used instead of a pure capacitor. Therefore, in the electrical circuit (Fig. 7a), R_s is the solution resistance, Q_{dl} (CPE_{dl}) is the double-layer CPE, R_{ct} is the charge transfer resistance, Q_{coat} (CPE_{coat}) is the coating CPE, and R_{po} is the coating pore resistance. The CPE impedance is determined by Eq. (1):

$$Z_{CPE} = \left[Y_0(j\omega)^n\right]^{-1} \quad (1)$$

where Y_0 is the CPE magnitude, j is the imaginary number, ω is the angular frequency (rad/s), and n is the deviation parameter from the ideal behavior of a pure capacitor. For n = 1 and n = 0, the CPE behaves like an ideal capacitor and an ideal resistor, respectively.

According to Fig. 6, there is only one time constant for the coatings having 20 wt% doped microcapsules (unscratched) and the neat coating (unscratched and without microcapsules). Thus, according to the published literature[8, 37] the equivalent circuit shown in Fig. 7b was used and the extracted electrochemical

data are presented in Table 3. There are three components in this electrical circuit model, consisting of solution resistance (R_s), coating pore resistance (R_{po}), and constant phase element (Q_c) as shown in Fig. 7b.

The highest corrosion resistance was observed for the 20 wt% embedded-microcapsules coating (R_{po} = 27.4 kΩ.cm^2) among its counterparts and the neat coating (R_{po} = 4.0 kΩ.cm^2). The coating's corrosion resistance with 20 wt% microcapsules was about 7 and 22 times more than the neat coating and the bare steel (R_{ct} = 1.2 kΩ.cm^2) respectively; indicating the improvement of the barrier properties of the coating in the presence of microcapsules. The resistivity of the scratched neat coating is approximately 3 times higher than of the bare steel. This can be due to the swelling of the coating cut edges or the corrosion products in the cracked area, which provide a barrier against ions and improve the coating resistivity.

By considering the data presented in Fig. 5 and Table 2, it can be identified that the addition of the polyurethane microcapsules to the coating results in an increase in polarization resistance and total impedance. The healed-scratch area (either partially or completely) hinders and retards the corrosion reaction at the scratch site. One way to assess the healing performance is to compare the healing ability of the microcapsule-embedded coating with the neat one. Therefore, the healing efficiency of the coatings was precisely calculated via Eq. 2:

$$HealingEfficiency(\eta) = \left(\frac{R_{po/w} - R_{po/wo}}{R_{po/w}} \right) \times 100 \quad (2)$$

where the $R_{po/w}$ and $R_{po/wo}$ are the corrosion resistance associated with pore of the coating with and without the presence of microcapsules (in the presence of scratches), respectively. According to the data presented in Table 2, the polyurethane coating containing 20 wt% polyurethane microcapsules showed the most healing efficiency (85%). Although the microcapsule-embedded coating exhibited excellent healing ability, it could not repair the scratches completely. It can be explained by the fact that the exact amount of microcapsules in the damaged area is not predictable and providing enough healing material in the crack has always been a challenge in self-healing coating studies. Accordingly, it can be concluded in this study that the optimum microcapsules concentration was 20 wt%.

To investigate the effect of microcapsules and excess hardener on the barrier properties of the coatings, the EIS measurements were performed for the neat coating and the coating with 20 wt% microcapsules without any scratches. The plots are illustrated in Fig. 6 and the extracted data is presented in Table 3. It is clearly visible the unscratched neat and 20%-doped polyurethane coatings represent excellent corrosion resistance with R_{po}=110,500 kΩ.cm^2 and R_{po}=1,668 kΩ.cm^2, respectively. The corrosion resistance of the neat coating is more than the microcapsules-embedded coating. Therefore, it can be concluded that the presence of microcapsules and the excess hardener in the coating results in the loss of barrier properties,

It should be noted that the barrier property of the coatings is enhanced in the presence of released healing agent, although the healing agent could not seal the scratch entirely. In practical use, it is expected that the damaged area could be filled as much as possible. As can be seen from the data of the neat coating and the coatings containing different concentration of the microcapsules, it can be seen that although the presence of microcapsules enhances the barrier property of the coating in comparison with the neat coating (in the presence of scratches); it cannot completely restore and exhibit the original properties of a polyurethane coating without any defects. Wang and Zhou[37] reported that the weak force between new layer and the coating matrix could cause the failure of healed area.

The self-healing performance of the coatings containing polyurethane microcapsules can be clearly verified via SEM imaging. The SEM photomicrographs of the damaged region of the polyurethane coatings containing different concentrations of polyurethane microcapsules are shown in Fig. 8. The images demonstrate that the grooves of the scratched region are almost filled with the healing material, preventing the diffusion of the corrosive ions to the steel substrate. The healing performance directly relates to the amount of healing agent released into the damaged area. As can be seen, the coating with 30 wt% microcapsules could release a high amount of the healing agent into the crack zone. However, this feature cannot be enough to approve the best performance of coating. The high amount of microcapsules could provide more porosity and make pathways available for corrosive media to diffuse into the coating and affect the adhesion of the coating to substrate. By considering the data in Fig. 5, although more healing agent could be released in the damaged area, the best performance was achieved from the coating with 20 wt% microcapsules. Both SEM images and EIS data prove that the microcapsules are capable of releasing the healing agent and restoring the coating's damaged area. This typically indicates the role of the polyurethane resin in healing the inhomogeneity of the polyurethane coating, so the successful healing process is achieved.

Time Dependency of the Healing Process

For the sake of an effective healing performance, the healing agent should be released instantly when the possible cracks are generated.[3, 7] Impedance spectroscopy measurements were performed for the coating containing 20 wt% microcapsules with an X-cut thereon. The healing performance was evaluated by EIS within 48 hours at a certain time intervals. After every EIS test, the 3.5% NaCl solution within the scratch region was soaked up with a filter paper. The experimental plots are presented in Fig. 9 and the extracted electrochemical data are shown in Table 4. Based on the results, the highest corrosion resistance was obtained after 24 hours (R_{po}=37.9 kΩ.cm^2); hence the microcapsules released the most possible amount of polyurethane and sealed the scratches 24 hours after the cracks were created. In order to compare the time dependency of the healing efficiency at different time intervals, Eq. 3 was employed:

Table 4
The resulted electrochemical data after curve fitting the impedance data for the carbon steel coated with polyurethane resin containing 20 wt% polyurethane microcapsules in 3.5% NaCl electrolyte at different time intervals.

Time Intervals (h)	CPE Coat			CPE Double Layer			
	Q_c			Q_{dl}			
	R_{po} ($k\Omega.cm^2$)	$Y_0 \times 10^{-6}$ ($S^n.\Omega^{-1}.cm^{-2}$)	n	R_{ct} ($k\Omega.cm^2$)	$Y_0 \times 10^{-6}$ ($S^n.\Omega^{-1}.cm^{-2}$)	n	Efficiency η' (%)
1	11.8	221	0.79	1.3	276	0.59	
3	12.9	268	0.80	1.5	301	0.60	8
6	23.4	388	0.82	2.7	420	0.62	50
9	33.2	456	0.85	5.1	489	0.65	64
24	37.9	499	0.86	5.4	580	0.65	68
48	38.2	423	0.90	5.8	432	0.64	69

$$Time-dependent Healing Efficiency\left(\eta^{'}\right)=\left(\frac{R_{po/H}-R_{po/1H}}{R_{po/H}}\right)\times 100$$

3

where $R_{po/H}$ and $R_{po/1H}$ are the corrosion resistance of the coating pores at different time intervals and after one hour, respectively. In fact, $R_{po/1H}$ was selected as a reference because the healing agent was observed after 1h during the tests. According to the data presented in Table 4, it can be observed that after 6 hours, the healing efficiency was achieved a reasonable value of 50% and was increased to 68 % after 24 hours. Besides, there was a rise in time-dependent healing efficiency up to 48 hours. However, the increase in healing efficiency after 24 hours is insignificant which may be associated with the end of curing reaction between the released polyurethane resin and the curing agent available within the coating matrix.

Corrosion Performance of the Investigated Coating

To investigate the corrosion performance of coatings during healing process and exposure to the corrosive medium, carbon steel samples were coated with polyurethane resin containing 20 wt% polyurethane microcapsules. The surfaces of the coatings were scratched and then after 24 hours and mples were immersed in 3.5 % NaCl test

solution. After that, their corrosion resistance was evaluated within 7 days (168 hours) of exposure. The obtained Nyquist, Bode, and Bode phase plots are illustrated in Fig. 10 and the resultant electrochemical data are presented in Table 5. According to the EIS plots and the data, it is demonstrated that even after 7 days of immersion, the coating demonstrates a reasonable impedance. The data in Tables 2 and 5 proves the self-healing phenomenon in the damaged region, which successfully protect the steel substrate from the penetration of the corrosive ions since the corrosion resistance of the coating with 10 wt% microcapsules is about 3 times more than the scratched coating without microcapsules (R_{po}= 4.0 $k\Omega.cm^2$). It can be concluded that the self-healing coatings exhibit better corrosion resistance than the scratched coating without microcapsules. This resistance enhancement proves the healing phenomenon occurred even partially in some areas. The Bode plots (Fig. 10a) indicate the decrease in the total impedance of the investigated coatings versus exposure time; however, this decrease is not significant up to 48 hours as the coating shows stable corrosion resistance. As the immersion time increases over than 48 hours, the charge carrier ions diffuse through the scratched area of the coatings, which results in a noticeable decrease in corrosion resistance after 48 to 168 hours; it corresponds to the diameter of the semi-circle in Nyquist plots. According to Fig. 10c, the diameter of the semi-circle in the Nyquist plots indicates a noticeable decrease after 48 hours by increasing the immersion time. Besides, during the application of protecting coatings, intrinsic defects could be inevitably produced, providing a pathway for corrosive species through the coating layer. Consequently, these defects could profoundly affect the barrier properties of the coatings in the presence of a harsh environment.

Table 5
The extracted electrochemical data from EIS measurements to evaluate the corrosion performance of the carbon steel coated with polyurethane resin containing 20 wt% polyurethane microcapsules in 3.5% NaCl electrolyte at different time intervals.

Time Intervals (h)	CPE Coat				CPE Double Layer	
		Q_c			Q_{dl}	
	R_{po} ($k\Omega.cm^2$)	$Y_0 \times 10^{-6}$ ($S^n.\Omega^{-1}.cm^{-2}$)	n	R_{ct} ($k\Omega.cm^2$)	$Y_0 \times 10^{-6}$ ($S^n.\Omega^{-1}.cm^{-2}$)	n
1	37.9	391	0.80	4.6	411	0.75
24	43.7	319	0.79	5.2	376	0.70
48	38.8	387	0.80	4.7	430	0.76
168	9.0	2343	0.82	0.9	2761	0.75

Adhesion Test

The efficiency of the coatings is considerably influenced by their adhesion to the substrate. There could be a possible decrease in adhesion of polyurethane coating to the metallic substrate due to the addition of the microcapsules to the coating. The results of the adhesion test revealed that the coatings with 10 and 20 wt% microcapsules show the highest degree of adhesion equivalent to 5A. Nevertheless, the neat coating and the coating containing 30 wt% microcapsules reveal less adhesion to the substrate equivalent to 4A. Thus, according to these results, the presence of the microcapsules significantly increases the adhesion of the coatings. Furthermore, it can be concluded that the excessive concentration of the microcapsules (higher than 20 wt%) increases the coating porosity and hence decreases the water-resistance of the coating.[3]

Conclusions

This study investigated the healing ability of polyurethane coatings containing polyurethane microcapsules on carbon steel substrate. It was found that healing agent was successfully released from the microcapsules and restored the coating scratched area and enhanced the corrosion resistance of the polyurethane coating. The impedance and adhesion test revealed that coating containing 20 wt% microcapsules showed the best healing efficiency (85%) and adhesion to the substrate among its counterparts. The examination of the time dependency of the healing performance illustrated that the healing efficiency reaches the maximum value after 24 hours exposure to the test solution. The investigation of the corrosion performance revealed that the coatings containing microcapsules indicated excellent corrosion resistance up to 48 hours, though the resistance ability of the coatings decreases slightly after 48 hours. Accordingly, the polyurethane microcapsules could extend the service life of the polyurethane coatings and show promise in self-healing applications.

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Figures

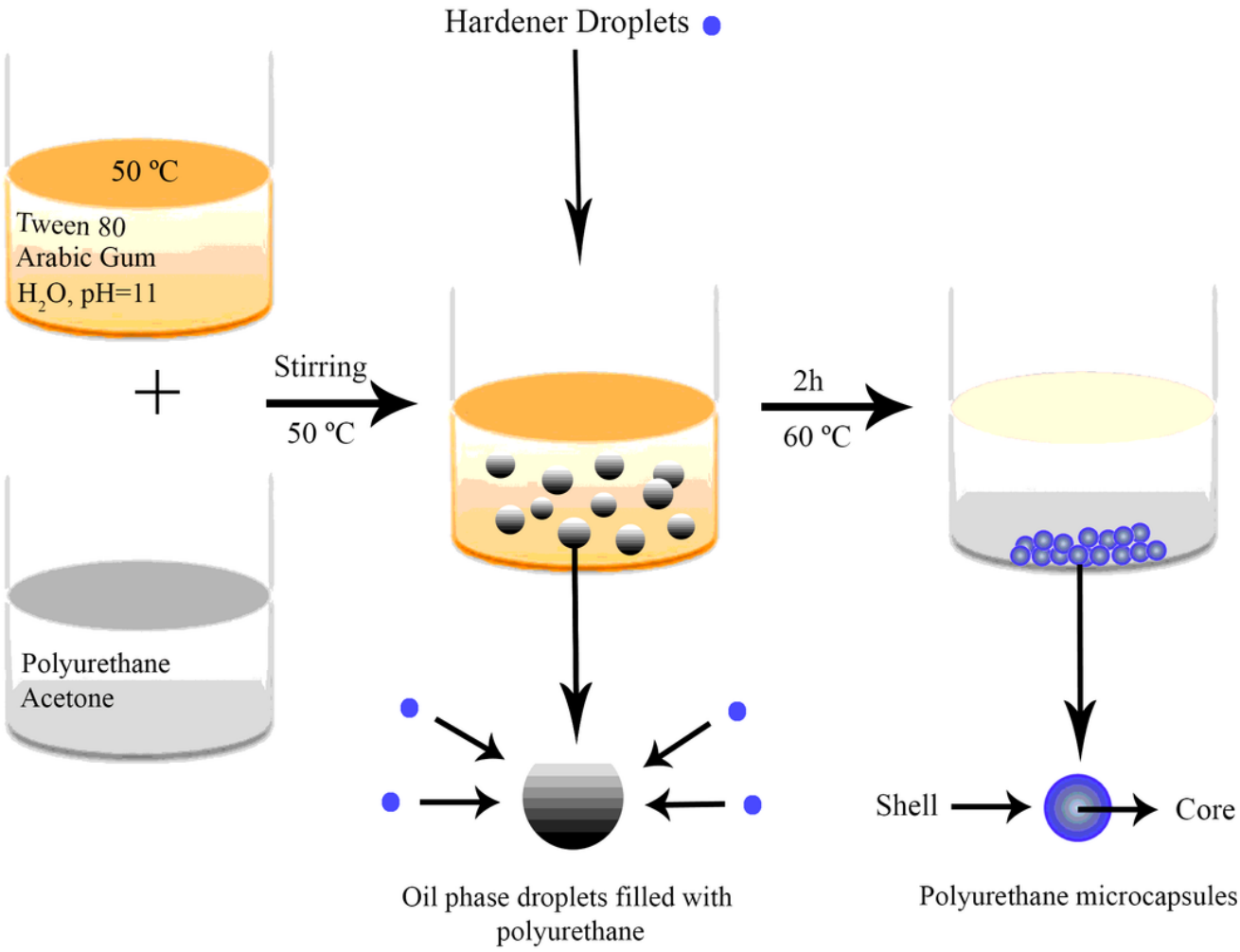

Figure 1

The schematic of the microcapsules' fabrication process.

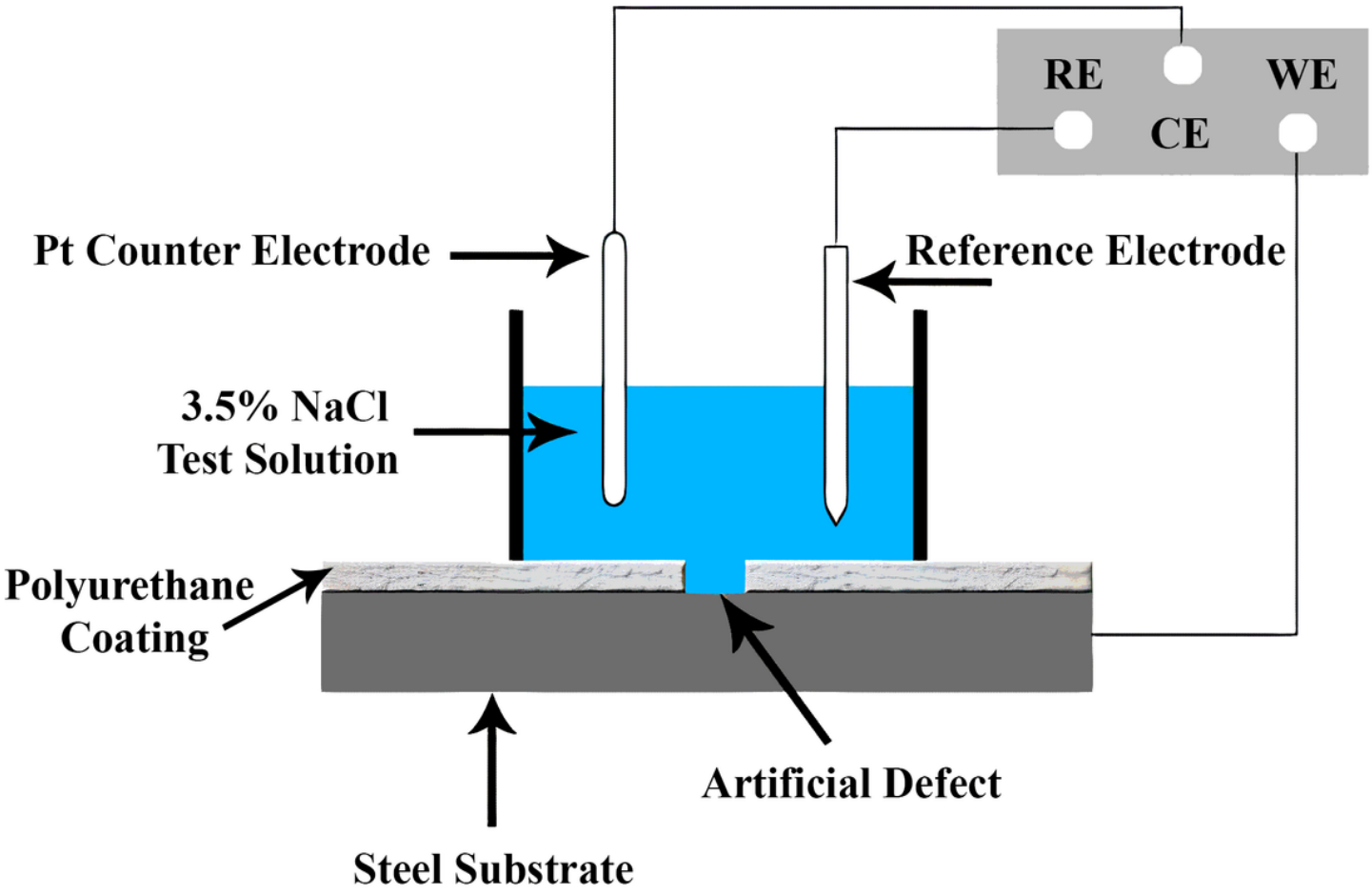

Figure 2

Schematic view of the employed electrochemical cell.

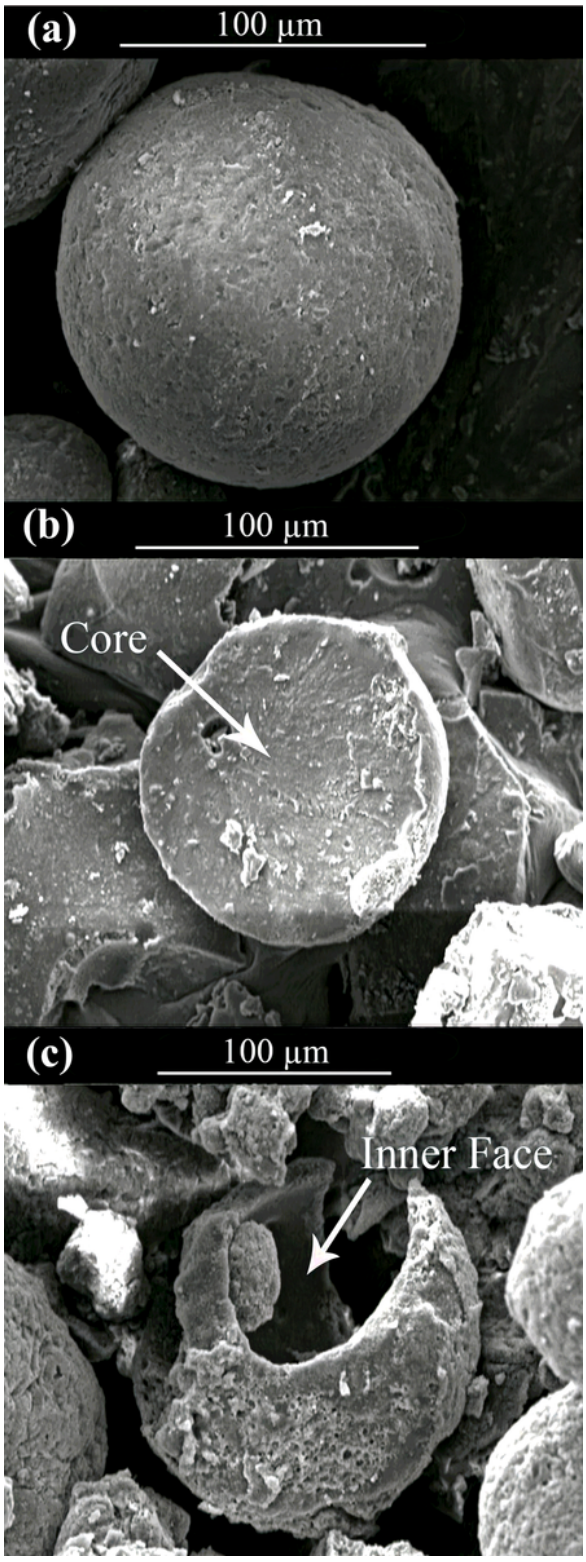

Figure 3

SEM images of the synthesized polyurethane microcapsules; a). A view of the synthesized microcapsule; b) the crushed microcapsule; c). Inner face and the shell thickness.

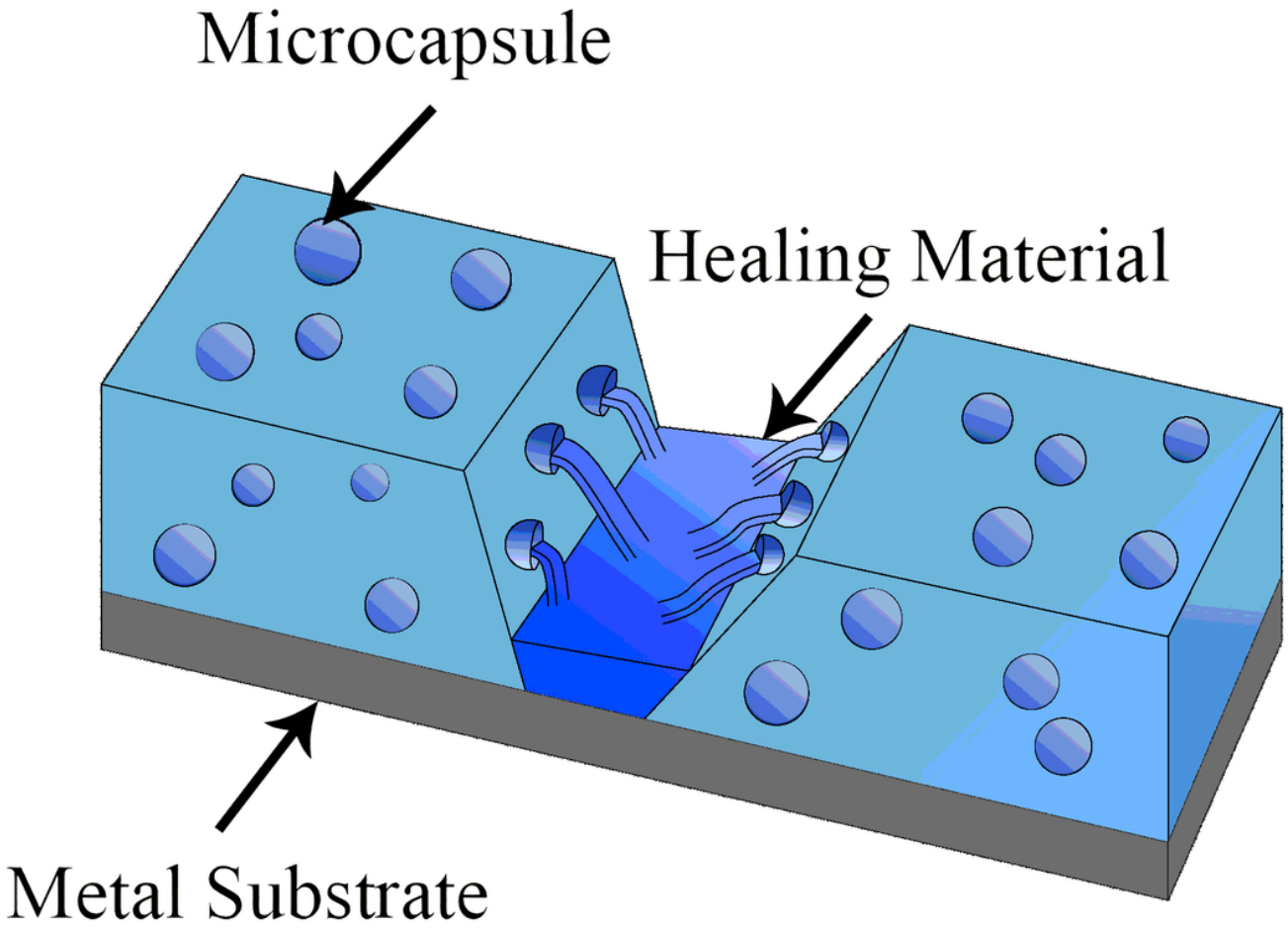

Figure 4

Schematic view of the healing process via micro-encapsulation technique within the coating matrix.

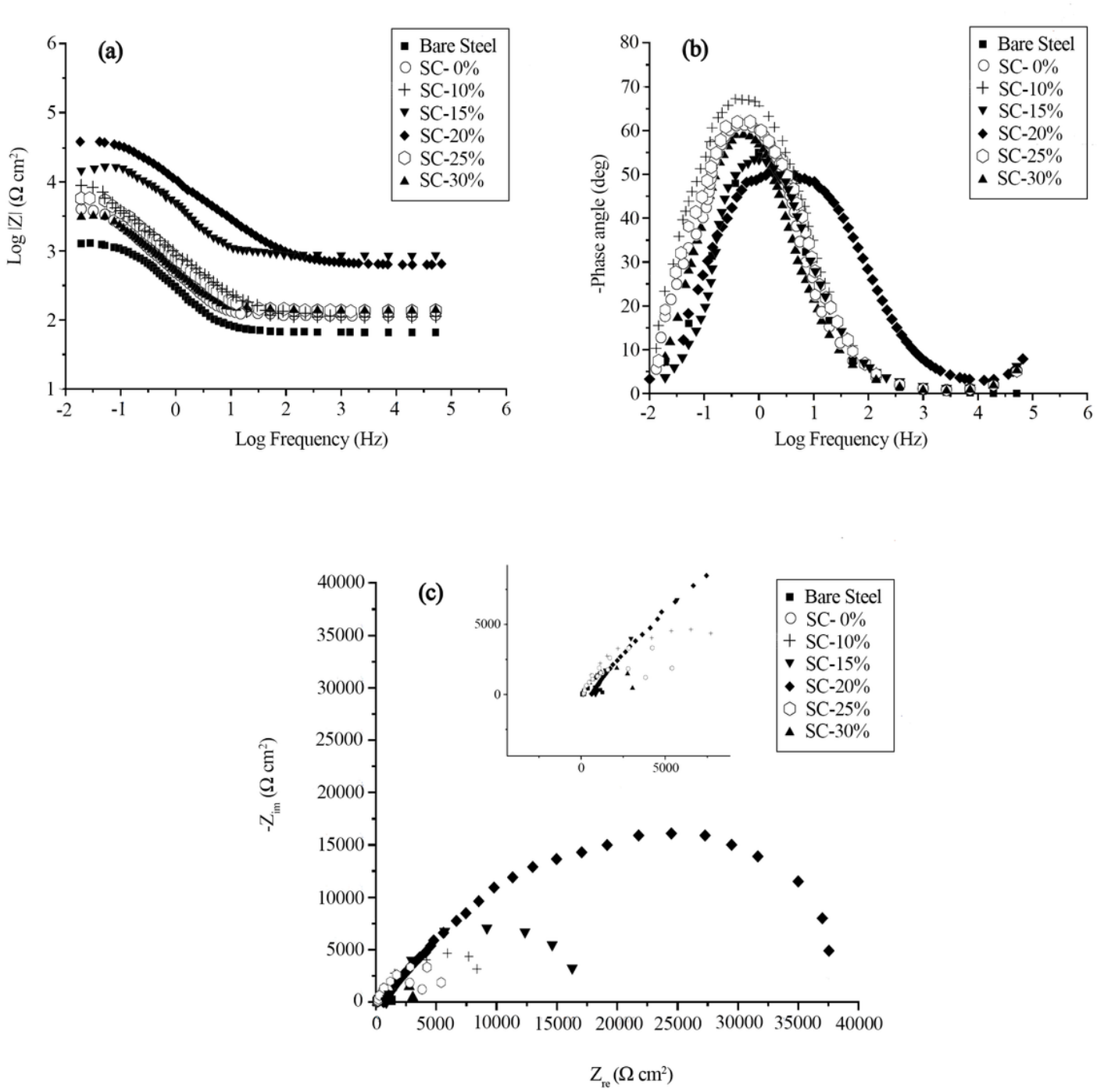

Figure 5

Electrochemical impedance results for the carbon steel samples coated with polyurethane resin containing different concentrations of polyurethane microcapsules with scratches in 3.5% NaCl electrolyte; a). Bode magnitude; b). Bode phase; c). Nyquist plots.

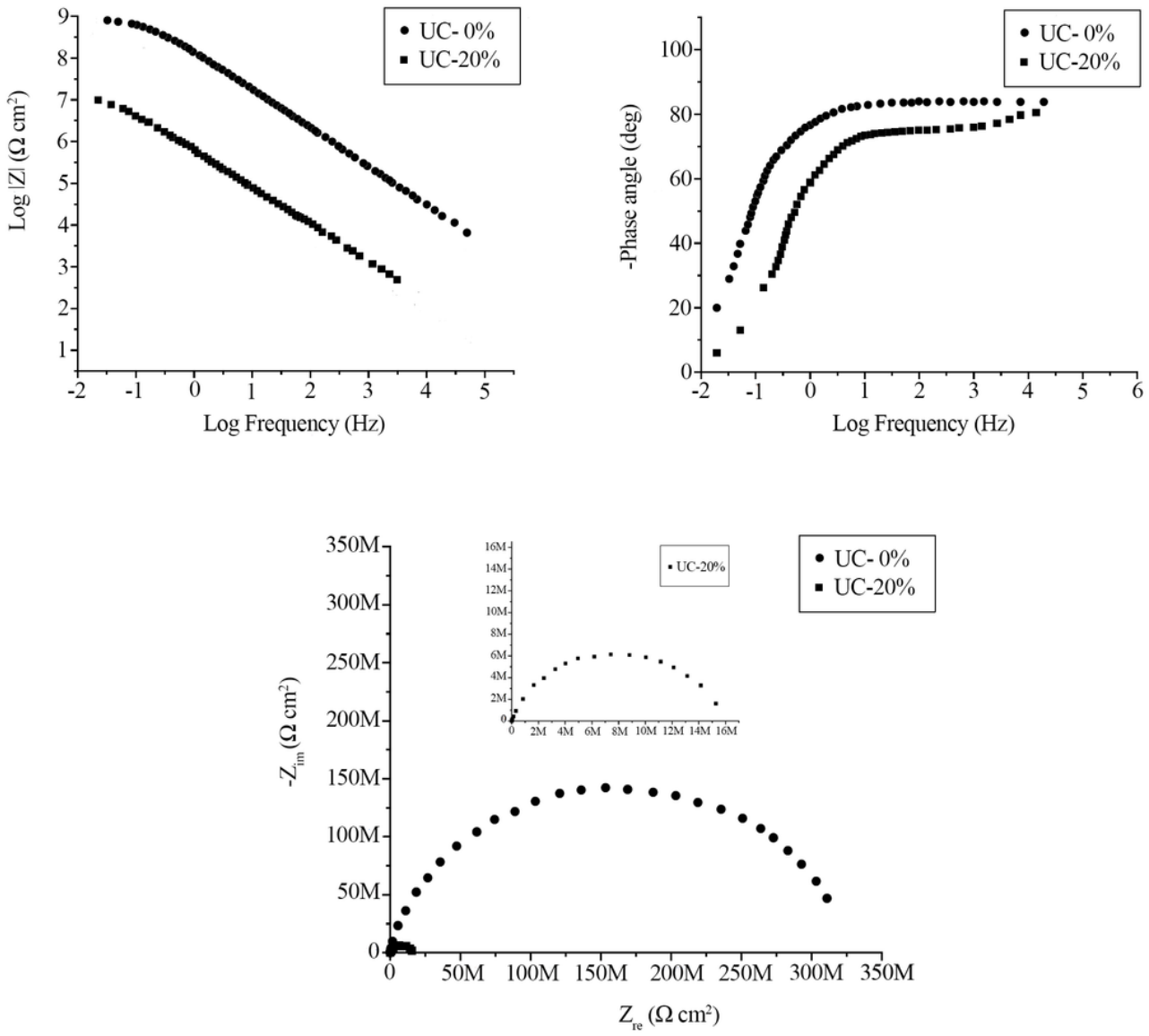

Figure 6

Electrochemical impedance results for the carbon steel coated with polyurethane resin containing 20 wt% polyurethane microcapsules and the neat coating (absence of microcapsules) without scratches in 3.5% NaCl electrolyte; a). Bode magnitude; b). Bode phase; c). Nyquist plots.

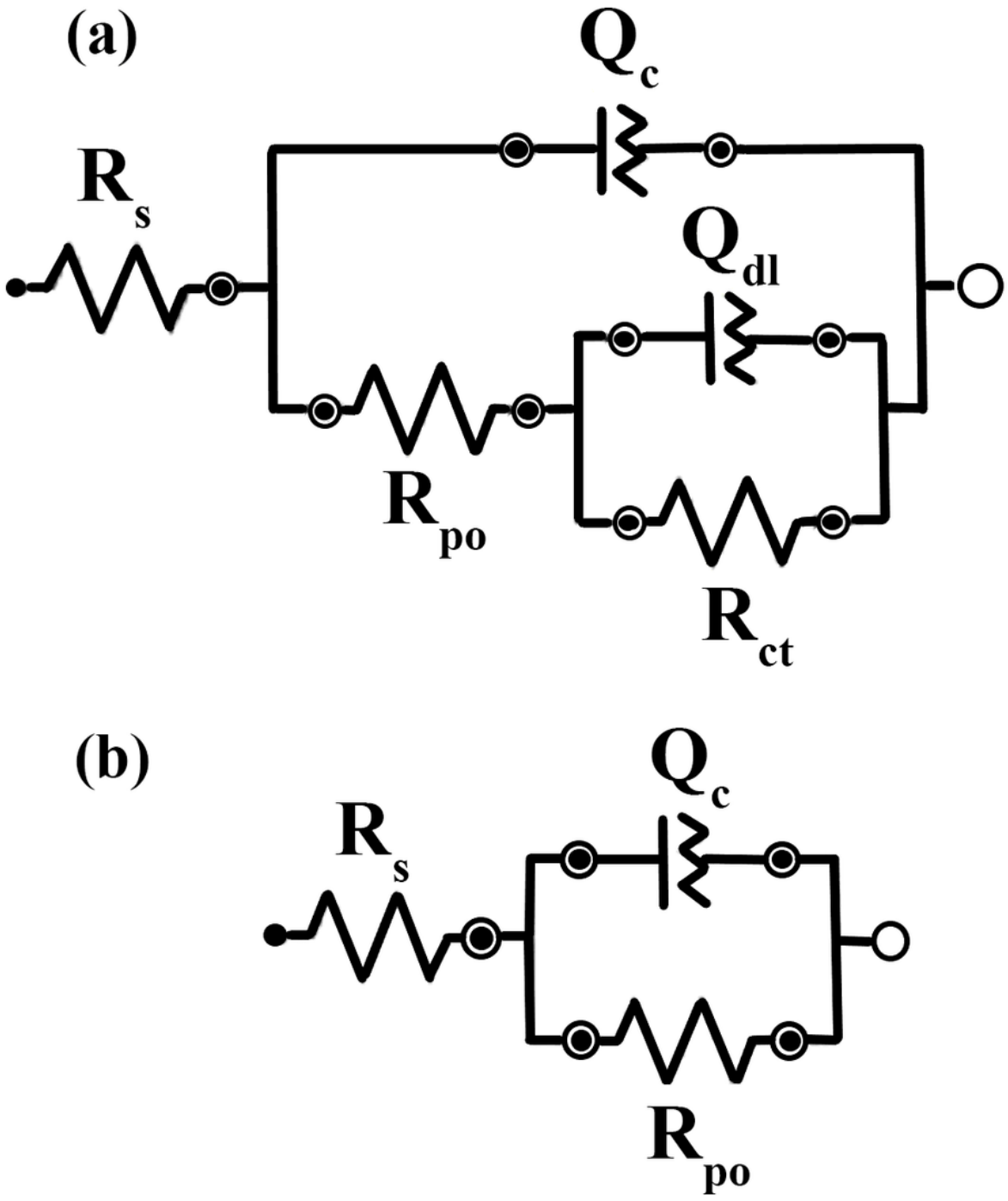

Figure 7

The equivalent circuit models.

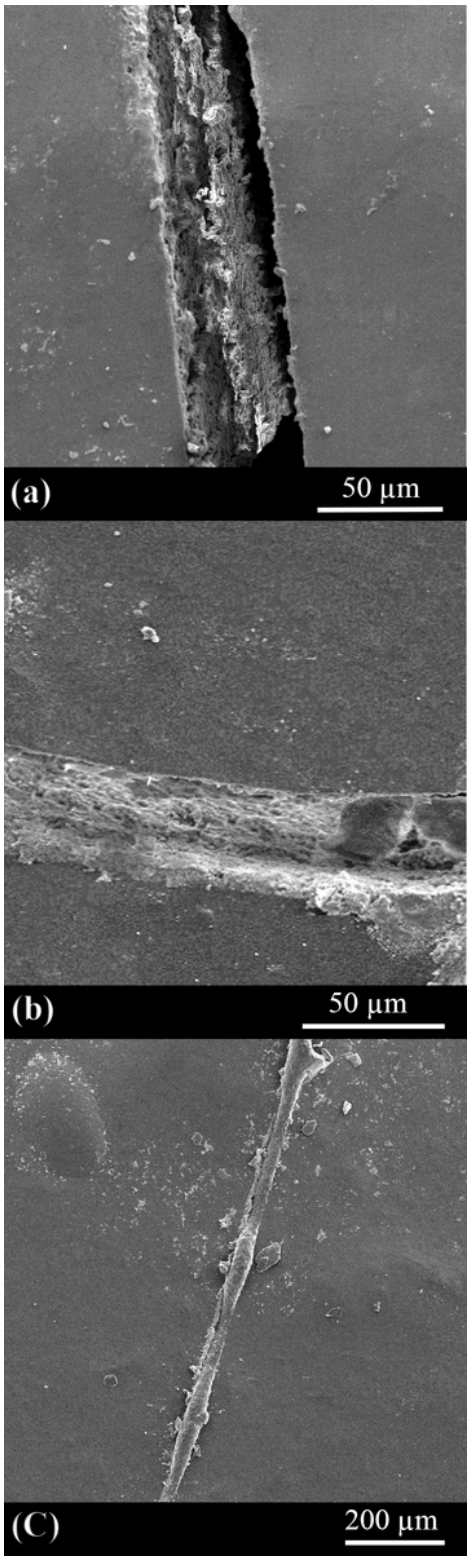

Figure 8

The SEM surface photomicrographs of the healed damaged area of the investigated polyurethane coatings; a). Containing 10 wt% microcapsules; b). Containing 20 wt% microcapsules; c). Containing 30 wt% microcapsules.

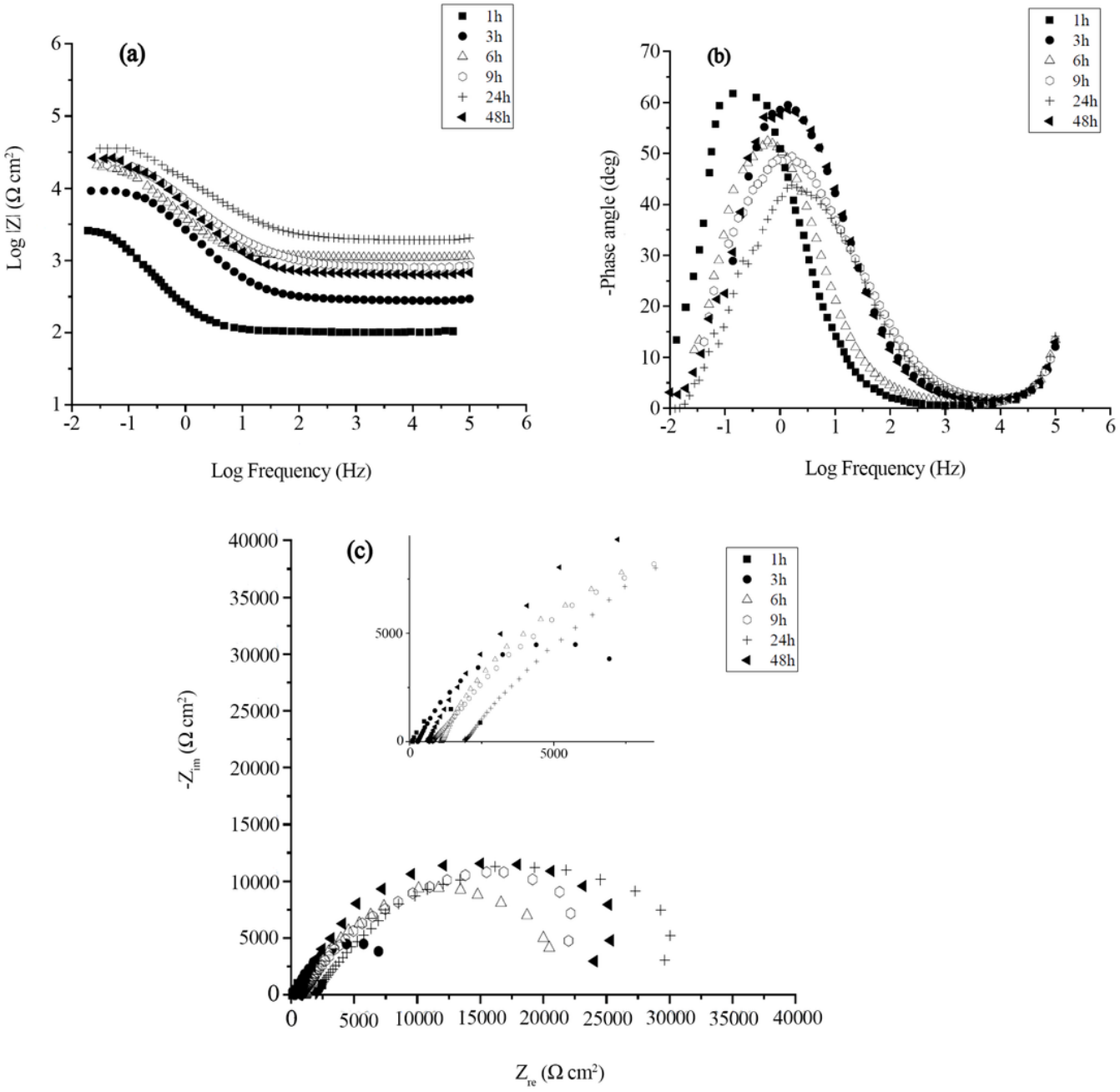

Figure 9

Electrochemical impedance results for the carbon steel coated with polyurethane resin containing 20 wt% polyurethane microcapsules in 3.5% NaCl electrolyte at a certain intervals of 48 hours after being scratched; a). Bode magnitude; b). Bode phase; c). Nyquist plots.

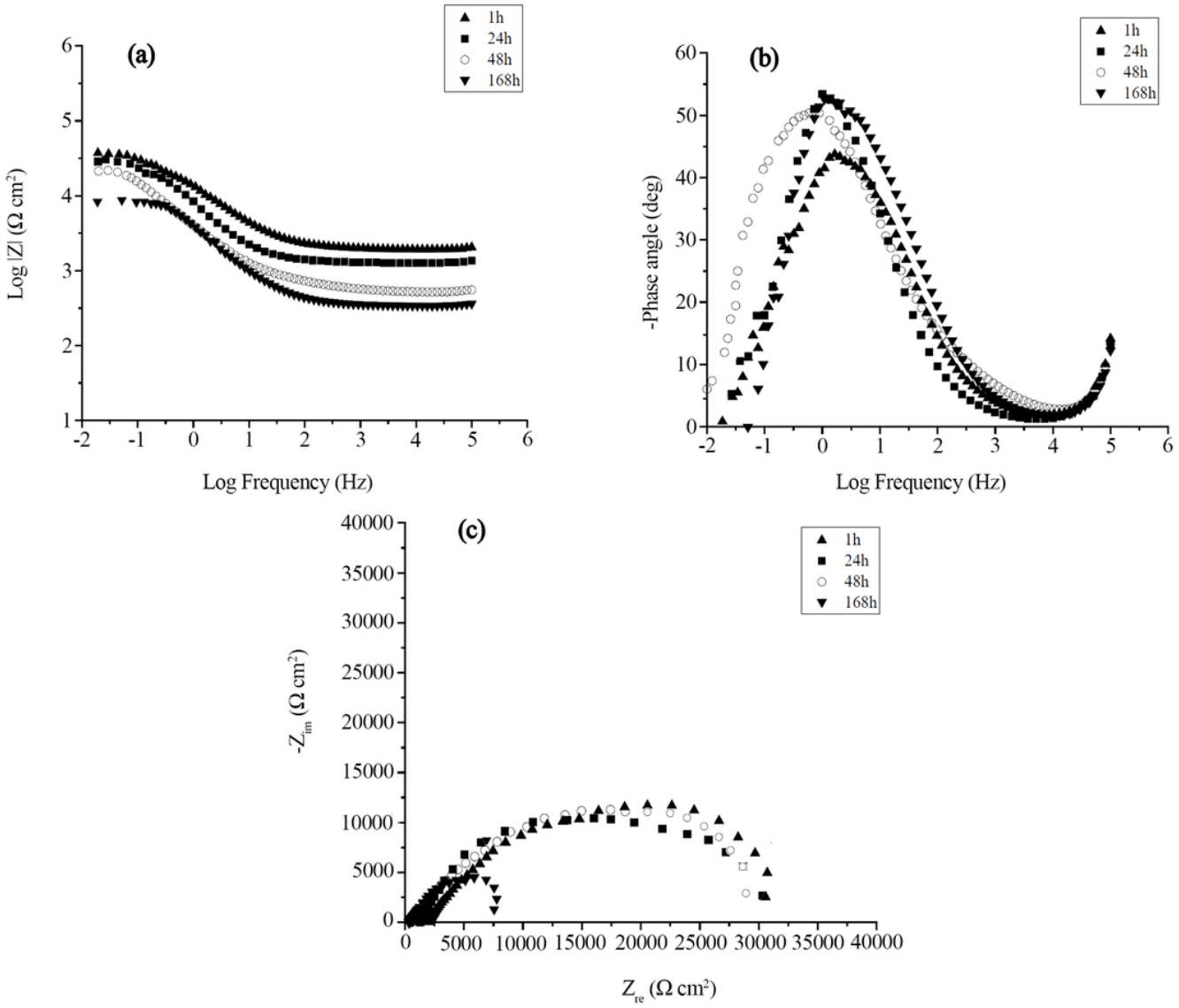

Figure 10

Electrochemical impedance results for the carbon steel coated with polyurethane resin containing 20 wt% polyurethane microcapsules in 3.5% NaCl electrolyte at a certain time intervals of following 7 days, after 24 hours of being scratched and healed; a). Bode magnitude; b). Bode phase; c). Nyquist plots.