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Fabrication of Various Epoxy Coatings for Offshore Applications and Evaluating Their Mechanical Properties and Corrosion Behavior

Mohammad Asif Alam[1], *El-Sayed M. Sherif* [1,#,*], *Saeed M. Al-Zahrani* [1,2]

[1] Center of Excellence for Research in Engineering Materials (CEREM), Advanced Manufacturing Institute, King Saud University, P. O. Box 800, Al-Riyadh 11421, Saudi Arabia
[2] SABIC Polymer Research Center (SPRC) and Department of Chemical Engineering, College of Engineering, King Saud University, P.O. Box 800, Al-Riyadh 11421, Saudi Arabia
[#] On leave from Electrochemistry and Corrosion Laboratory, Department of Physical Chemistry, National Research Centre (NRC), Dokki, 12622 Cairo, Egypt
[*]E-mail: esherif@ksu.edu.sa; emsherif@gmail.com,

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This work reports the mechanical properties and corrosion performance of a newly fabricated series of protective epoxy coatings for offshore applications. Bisphenol A diglycidyl ether epoxy resin (DGEBA) was treated with different stoichiometry variations of polyamidoamine adducts (ARADUR-PA450) as a curing agent at ambient temperature to fabricate four different formulations of epoxy coatings (DGEBA-PA450). The cured epoxy coatings were applied on glass and steel substrates for mechanical and corrosion characterizations, respectively. Mechanical tests were performed for the coated glass samples using scratch tester, mandrel bend, cross hatch tester, and pendulum hardness measurements. Fourier-transform infrared spectroscopy attenuated total reflectance (FT-IR-ATR) was employed to report the composition of the fabricated coatings. The coated steel coupons were immersed for 1 h and 7 days in aerated stagnant solutions of 3.5% NaCl and corrosion test was conducted using electrochemical impedance spectroscopy (EIS) investigations. Collected results together indicated that all fabricated epoxy formulations can be used as protective coatings against corrosive marine environments and that due to the high cross-linking of the amino group of the polyamidoamine adducts ARADUR 450 at ambient temperature.

Keywords: epoxy coatings, polyamidoamine adducts, corrosion resistance, mechanical properties, electrochemical impedance spectroscopy

1. INTRODUCTION

Coatings impart specific engineering properties of a substrate material by modifying or applying a thin layer at its surface. One of the most important methods and is considered as the first line defense in the protection of metal and alloy structures against corrosion in corrosive environments is the use of protective coatings [1-4]. Therefore, the driving force for the advancement in the industry of coatings has been an improvement in corrosion and wear resistances. The aim has been to enhance reliability and performance of various structural components to enable them to resist corrosion, pitting, exfoliation, erosion, sliding and wear. Corrosion and wear resistant coatings can be used in a variety of industries such as in automobile, power generation, utility, aerospace, defense, optical equipment, magnetic storage devices and bearings, engine parts and seals, etc [5-11].

Organic coatings are commonly used to protect metallic structures against corrosion due to their high barrier and superior mechanical properties. Although there are many coating systems such as polyurethane, acrylic coatings, vinyl based coatings etc, available in the market, epoxy coatings system plays a vital role in marine coating industries [12]. Several curing agents e.g. polyamide, polyamine, polyamidoamine, etc., are often used for epoxy applications. Frequently, most of the companies update their products with new resin and hardener combination. The performance of epoxy curing system is affected primarily by molecular weight of the epoxy resin and concentration of curing agent [13]. Thus, it is mandatory to analyze or identify a unique combination of curing agent and epoxy resin to enhance the desired properties.

The epoxy coatings are the common victim of surface abrasion and poor resistance to the initiation and propagation of cracks [14]. Such processes propagate defects in the coating and impair their appearance and mechanical strength. The defects can act as pathways accelerating the diffusion of water, oxygen, and corrosive species onto the metallic substrate, resulting in its localized corrosion. Due to hydrophilic in nature, epoxy coatings experience large volume shrinkage upon curing and can absorb water from surroundings [15]. The presence of pores in the cured epoxy coating can assist in the migration of absorbed water and other species to the epoxy–metal interface leading to the initiation of corrosion of the metallic substrate and to the delamination of the coating [16]. It has been reported [17] that higher cross-linking density increases the anticorrosion behavior by decreasing the free volume and segmental mobility in the coating. It is difficult for the aggressive molecules to penetrate through the coating.

In the current work, various epoxy coating formulations were developed with optimized quantity of polyamidoamine adducts ARADUR-PA450 to obtain high performance for corrosion resistance applications. The optimization was performed based on the different stoichiometric ratios of the curing agent. Different characterization procedures were followed to identify the performance of coatings such as pendulum hardness, scratch test, mandrel bend test, cross hatch test, and FTIR-ATR techniques. The corrosion resistance after 1 h and 7 days immersion in 3.5% NaCl solutions was investigated using electrochemical impedance spectroscopy.

2. EXPERIMENTAL PROCEDURE

Bisphenol A diglycidyl ether epoxy resin (DGEBA, Hexion Chemicals), polyamidoamine adducts ARADUR 450 (PA450, Huntsman Advanced Materials), acetone (Merck, 99%), xylene (Merck, 99%), methyl isobutyl ketone (MIBK, Merck), and sodium chloride (NaCl, Merck, 99%).

Glass and steel plates were used as the coated substrates in order to perform the different characterization measurements

The epoxy coating formulations were developed using DGEBA epoxy resin, different percentages of the PA450 hardener, and compatible solvents of xylene and MIBK in addition to an air releasing agent. The resin was stirred at 500 rpm in a dispermat mixer (BYK Gardener, Germany) for 5 min and solvents were gradually mixed at the same speed. The air releasing agent was added drop by drop during the initial mixing period to achieve homogeneous mixing with other solvents of xylene and MIBK. Finally, the hardener was mixed at 1000 rpm, before applying the formulations on the substrate like glass plates and different sizes of the steel plates depending on the required characterization technique. The chemical compositions for the different fabricated DGEBA-PA450 epoxy coatings are listed in Table 1.

The gloss measurements for the different samples were performed using a tri-gloss meter, Sheen Instruments Co (U.K). The Tri-gloss meter was provided with standard geometries of 20°, 60° and 85°. The film thickness was measured using an Ecotest plus instrument (Sheen Instruments Co., (UK). Koenig hardness was measured using pendulum hardness rocker (Sheen Instruments Co., UK). The scratch, flexibility and adhesion measurements were carried out using scratch tester, mandrel bend and cross hatch testers (Sheen Instruments Co., UK), respectively.

Table1. Chemical compositions for the different fabricated DGEBA-PA450 epoxy coatings.

Epoxy coating	Composition					
	PA450	Air release	Xylene	MIBK	DGEBA	Stoichiometry
E-1	19.98	0.2	20	20	80.02	+10
E-2	18.16	0.2	20	20	81.84	0.0*
E-3	16.34	0.2	20	20	83.66	-10
E-4	14.53	0.2	20	20	85.47	-20

* indicates the stoichiometric ratio.

An electrochemical cell with a three-electrode configuration was used; a coated steel, a stainless steel, and an Ag/AgCl electrode (in saturated KCl solution, Metrohm 6.0724.140), were used as the working, counter, and reference electrodes, respectively. The steel substrates were prepared by polishing and then rinsing with acetone. The different epoxy coatings were applied on the steel panels using film applicator. The coated samples were then dried at room temperature for curing.

Fourier-transform infrared spectroscopy (FTIR-ATR) analyses were performed using a Fourier transform (Perkin Elmer, UK) and the data were collected over two wavenumber ranges, i.e. 500 – 2000 cm^{-1} and 500 – 4000 cm^{-1}, respectively. Electrochemical impedance spectroscopy (EIS) experiments were performed by using an Autolab Potentiostat (PGSTAT20 computer controlled) operated by the general purpose electrochemical software (GPES) version 4.9. EIS spectra were collected at an open circuit potential after 1 h and 7 days immersion in a stagnant open to air 3.5% NaCl solution over a frequency range from 10,000 to 0.01 Hz, with an ac wave of ± 5 mV peak-to-peak overlaid on a dc bias potential, and the impedance data were collected using Powersine software at a rate of 10 points per decade change in frequency. All measurements were carried out at room temperature using two samples to obtain statistically significant results.

3. RESULTS AND DISCUSSION

3.1. Mechanical properties of the epoxy coatings

In order to study the effect of the different stoichiometry variations of polyamidoamine adducts ARADUR 450 hardener on the mechanical properties of DGEBA-PA450 epoxy coating, the Koenig hardness, dry film thickness, scratch resistance load, mandrel bend, cross hatch, and gloss measurements have been carried out. Table 2 shows the mechanical properties of the different DGEBA-PA450 epoxy coatings. The Koenig hardness of DGEBA-PA450 epoxy coatings in the presence of different additives and polyamidoamine adducts ARADUR 450 hardener was determined by a dry film thickness of 60-80 μm on glass substrates. According to ASTM standards, a layer of at least 25 μm thicknesses is required to minimize the influence of the substrate. It is clearly seen from Table 2 that the minimum recorded hardness value for EDGEBA-PA450 system was 122 for E-3 coating and the highest value was 149 for E-2. It has been reported [18] that the hardness value is directly related to the proportion of cross-linking between epoxide groups and curing agents. This means that the cross linking between the DGEBA groups and PA450 hardener is the highest at the stoichiometry ratio of the E-2 epoxy coating.

The scratch resistant properties of the epoxy coatings with PA450 hardeners were determined with a dry film thickness of 60-80 μm on steel substrates. The highest scratch resistance for the different formulas was decreased in the following order; E-1 > E-3 > E-2 > E-4. The higher scratch hardness can also be correlated to the polar hydroxyls and oxirane moieties present in the backbone of the polymeric chain of the PA450 epoxy resin [19].

It is also seen from Table 2 that all the fabricated DGEBA-PA450 epoxy coatings passed the mandrel bend test perfectly. Cross-hatch tests also confirmed that all formulations had an excellent performance. Furthermore, the gloss measurements that were performed at two geometries, 20° and 60°, indicated that the measured values were consistent for all the DEGBA systems. According to Koleske [20], a greater gloss value than 70 (gloss unit, GU) at 60° for coatings should be measured again at 20°, which is more suitable and covers the majority of coatings applications. However, all our measured gloss values, whether were taken at 20° or 60°, showed a consistency for all fabricated coatings.

Table 2. Koenig hardness, dry film thickness, scratch resistance load, mandrel bend, cross hatch, and gloss measurements for the different DGEBA-PA450 epoxy coatings.

Epoxy coating	Measuring test						
	Koenig hardness after 15 days	Dry film thickness / µm	Scratch resistance load at mar failure / kg	Mandrel bend test	Cross hatch test	Gloss measurement at	
						20°	60°
E-1	128	60 ~ 80	6.5	Pass	Excellent	103 GU	102 GU
E-2	149	60 ~ 80	4.5	Pass	Excellent	91 GU	93 GU
E-3	122	60 ~ 80	6.0	Pass	Excellent	100 GU	101 GU
E-4	131	60 ~ 80	3.5	Pass	Excellent	100 GU	97 GU

3.2. Fourier-transform infrared spectroscopy attenuated total reflectance (FTIR-ATR) investigations

In order to ensure the homogenious dispersion of the epoxy coating with the hardener at the different stoichiometric variations and to identify the functional groups of the coatings' molecules, FTIR-ATR analyses were carried out on the surface of all fabricated epoxy coatings. Fig. 1 shows the FTIR-ATR spectra, which were taken for the dry surface of the different epoxy coatings. The spectra were collected at a wavenumber range between 500 and 4000 cm^{-1} to see the reflectance for every spectrum appeared from coatings surfaces. Because there are many peaks appear at the wavenumber range between 500 and 2000 cm^{-1}, the FTIR-ATR spectra were taken and plotted separately as shown in Fig. 2.

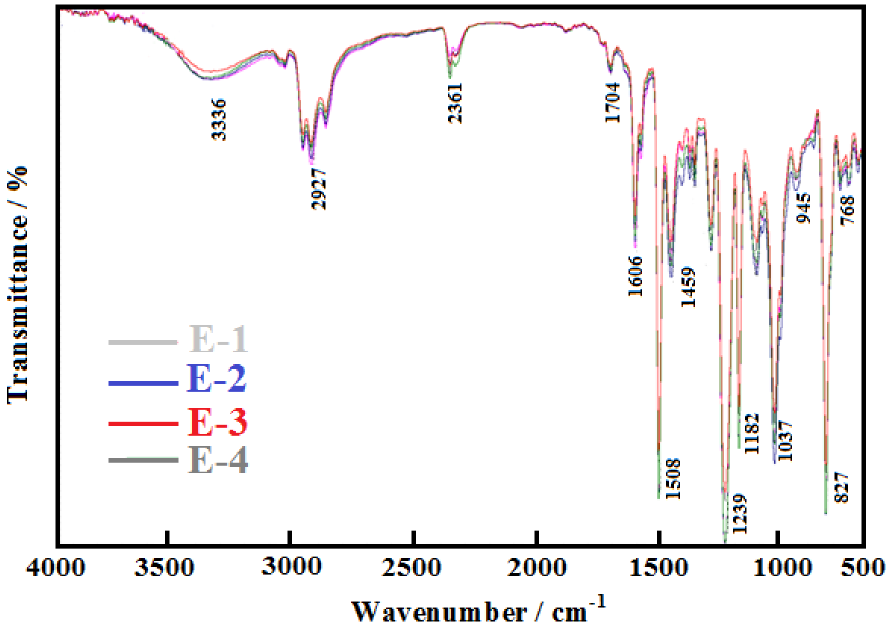


Figure 1. FTIR-ATR spectra obtained for the dry surface of the different glass epoxy coated surfaces at a wavenumber range between 500 and 4000 cm^{-1}.

The chemical structure of DGEBA molecule, as shown by Scheme 1, contains variety of organic groups such as aromatic rings, -CH_3, ≡C-O-C≡, etc. It has also been reported [21] that the polyamidoamine molecule (PA450) contains multi functional groups of -OH, -NH_2, -N=N-, =C=O, etc. A combination of DGEBA and PA450 with stoichiometric variations shown in Table 1 would probably lead to a compound that contains all of their organic and aliphatic groups. It is clearly seen from Fig. 1 and Fig. 2 that the all spectra showed the same peaks; 768, 827, 945, 1037, 1107, 1182, 1239, 1295, 1392, 1459, 1508, 1606, 1704, 2361, 2927, and 3336 cm^{-1}. The appearance of the peaks at 1606, 1508, and 1392 cm^{-1}, as well as those at 1400-1000 cm^{-1} resulted from aromatic rings [22-24]. Also, the C-H out-of-plane deformation vibration bands at 827 and 770-730 cm^{-1} are from the ring vibrations [23,24]. The broad band at 3336 cm^{-1} is mainly due to the O-H stretching of hydroxyl groups might form due to the formation of DGEBA-PA450 epoxy coating [23,24]. The only difference that is noticed from the FTIR-ATR spectra for the different epoxy coatings and can also be seen from Fig. 1 and Fig. 2 that the increase of the stoichiometric variation (Table 1) increases the intensity of the transmittance of the coating.

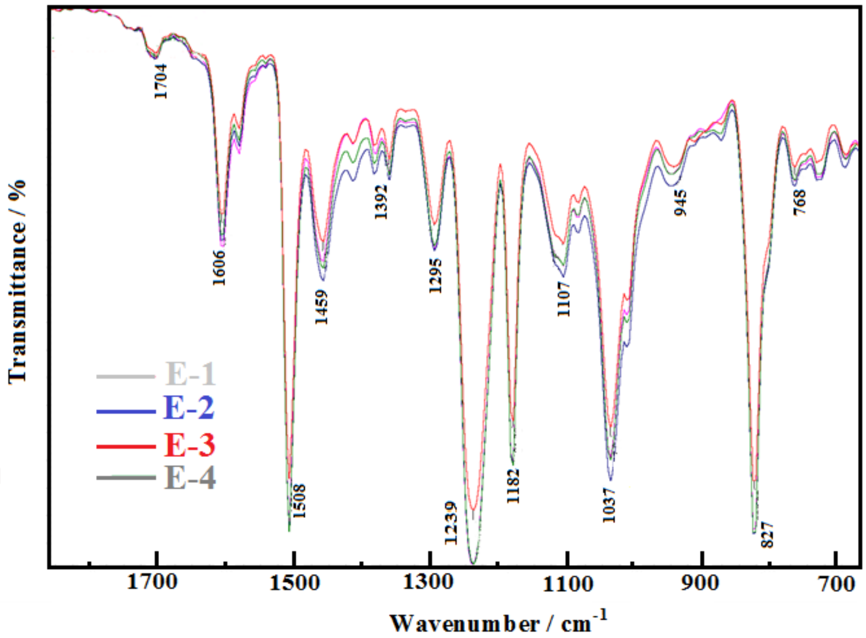
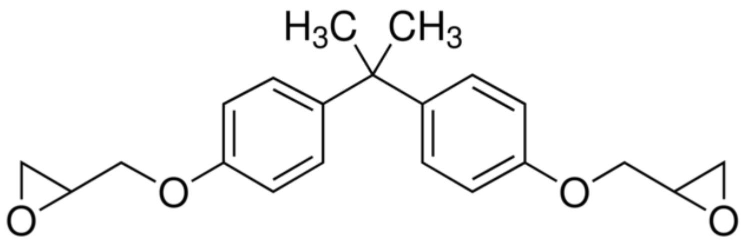


Figure 2. ATR-IR spectra obtained for the E-1, E-2, E-3, and E-4 of the glass epoxy coated surfaces at a wavenumber range between 500 and 2000 cm^{-1}.



Scheme 1. Chemical structure of the bisphenol A diglycidyl ether epoxy resin (DGEBA).

3.3. Electrochemical impedance spectroscopy (EIS) investigations

The EIS is a powerful technique that has been employed to explain the corrosion and corrosion protection of metals in corrosive media such as chloride solutions [25-40]. The EIS measurements in this study were carried out to determine kinetic parameters for electron transfer reactions at the interface of the coated steel coupons and the sodium chloride solution. Typical Nyquist impedance plots obtained for coated steel electrodes with (a) E-1, (b) E-2, (c) E-3, and (d) E-4 at an open-circuit potential after 1 hour immersion in 3.5 wt.% NaCl solutions are shown in Fig. 3. Similar plots were also obtained for the different epoxy coatings after 7 days immersion in the same solution as shown in Fig. 4. The Nyquist plots shown in Fig. 3 and Fig. 4 were fitted to the best equivalent circuit model as shown in Fig. 5. The values of the parameters obtained by fitting the equivalent circuit shown in Fig. 5 are listed in Table 3. According to usual convention, R_S represents the solution resistance between coated steel electrodes and the counter (stainless steel) electrode, Q_1 and Q_2 the constant phase elements (CPEs), R_{P1} the resistance of a film layer formed on the surface of the coated coupons, R_{P2} accounts for the polarization resistance at the coated coupons surface, and W the Warburg impedance.

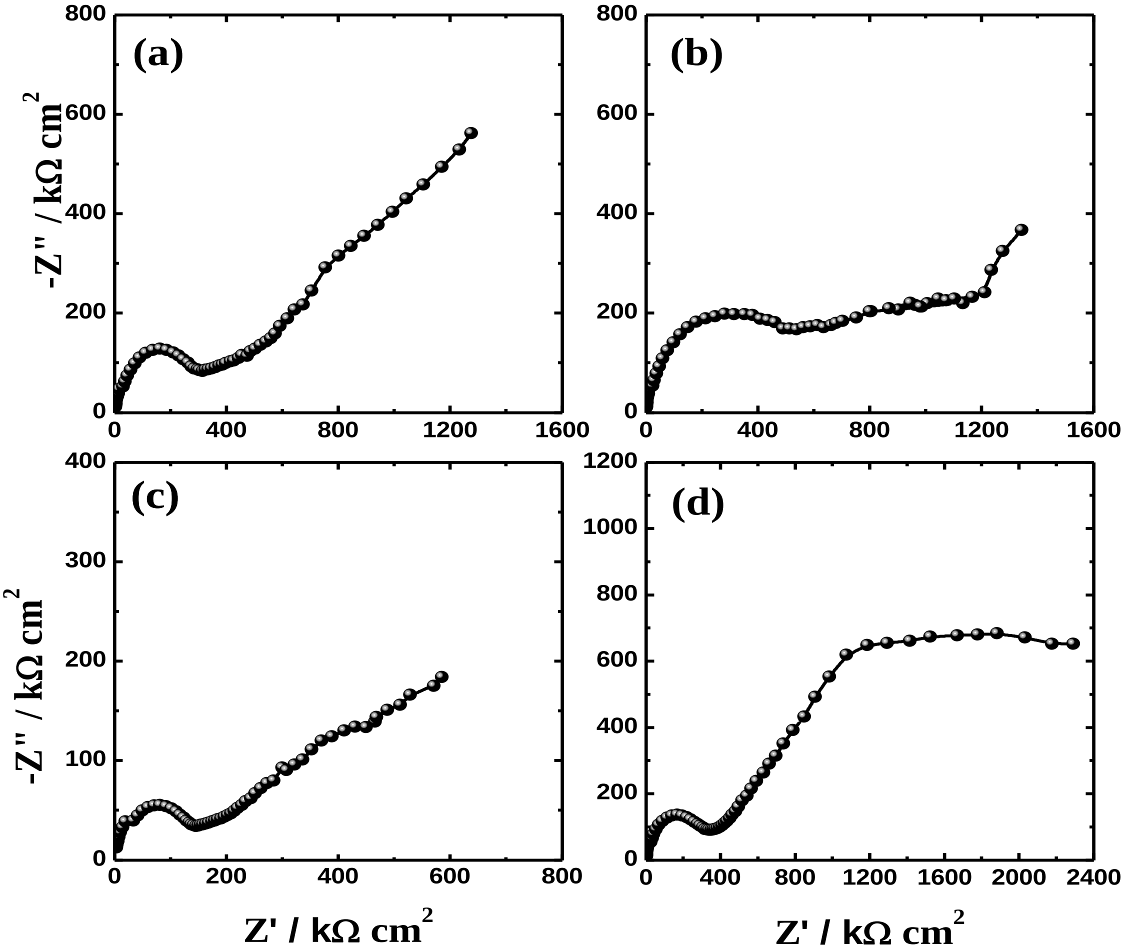


Figure 3. Typical Nyquist plots obtained for (a) E-1, (b) E-2, (c) E-3, and (d) E-4 epoxy coated steel respectively, after 1.0 h immersion in aerated stagnant 3.5 wt.% NaCl solution.

It is clearly seen from Fig. 3 and Fig. 4 that all the coated steel electrodes show a single semicircle followed by a segment; the bigger diameter for the semicircle as well as the larger the segment the higher corrosion resistance. It has been reported that [41-44] the semicircles at high frequencies are generally associated with the relaxation of electrical double layer capacitors and the diameters of the high frequency semicircles can be considered as the charge transfer resistance. This behavior for all coated steel samples indicates that all the fabricated epoxy coatings had the ability to decrease the electrochemical active and flawed areas on the steel substrate as a result of their being compact and adherent to the steel surface.

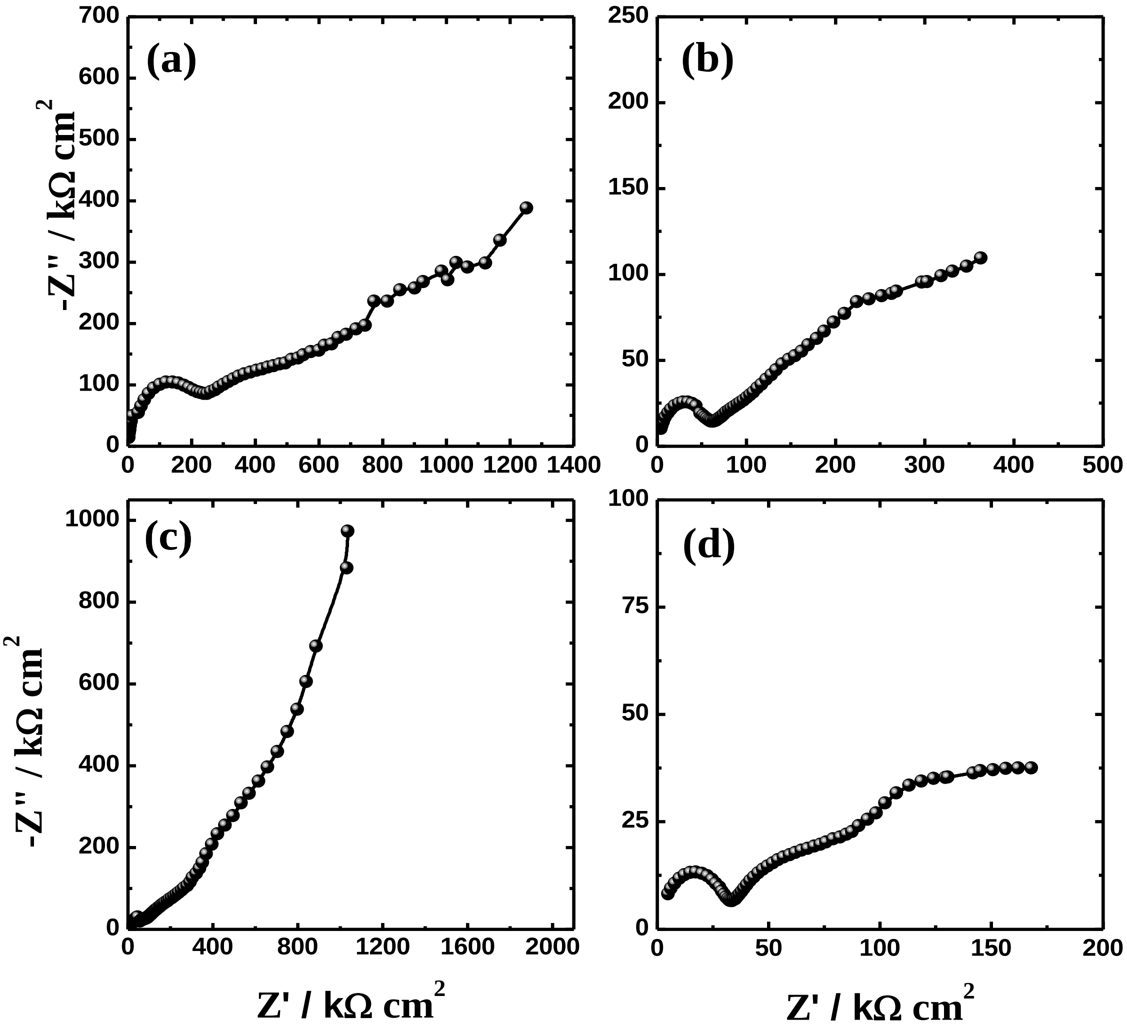


Figure 4. Typical Nyquist plots obtained for (a) E-1, (b) E-2, (c) E-3, and (d) E-4 epoxy coated steel respectively, after its immersion in aerated stagnant 3.5 wt.% NaCl solutions for 7.0 days.

It is also seen from Table 3 that the values of R_S, R_{P1} and R_{P2} recorded higher values for all the epoxy coatings. The higher the sum of the polarization resistances, $R_{P1} + R_{P2}$, the stronger is the resistance of coating against uniform corrosion rate. The CPEs, Q_1 with its n values almost 1.0 represent double layer capacitors. The CPEs, Q_2 with its n value is close to 0.5 represent Warburg (W) impedance. This is because depending on the value of n, CPE can represent resistance (Z(CPE) = R, n = 0), capacitance (Z(CPE) = Cdl, n = 1) or Warburg impedance for (n = 0.5). The presence of W in the equivalent surface indicates that if there is dissolution or degradation in the top coating layer will not occur by mass transfer. According to Kalenda [13] it was found that the stability of epoxy resins for corrosive electrolyte was hardened when sub theoretical amount of polyamine is considerably lowered. The highest corrosive electrolyte stability can be obtained in a range from the theoretical amount of polyamine to a system containing polyamine in an excess of 10 %. Such a low excess of polyamine can guarantee that in the state of gel, the last reacting groups meet.

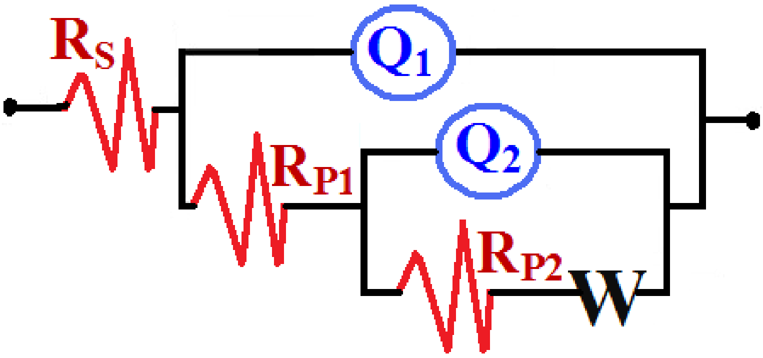


Figure 5. The equivalent circuit model used to fit the experimental data obtained for the epoxy coatings after their immersions in 3.5% NaCl solutions shown in Fig. 3 and Fig. 4.

Table 3. EIS parameters obtained by fitting the Nyquist plots shown in Fig. 3 and Fig. 4 with the equivalent circuit shown in Fig. 5 for the epoxy coatings immersed in 3.5% NaCl solutions for 1.0 h and 7.0 d, respectively.

.Epoxy coating	Parameter							
	R_S / Ω cm^2	Q1		R_{P1} / kΩcm^2	Q2		R_{P2} / kΩcm^2	W Ω S$^{-1/2}$
		Y_Q/ µF cm^{-2}	n		Y_Q/ µF cm^{-2}	n		
E-1 (1 h)	2196	3.11E-3	0.92	20840	1.487	0.49	11600	6.32E-9
E-2 (1 h)	4413	9.15E-3	0.94	38772	3.167	0.43	17122	4.03E-9
E-3 (1 h)	1915	1.72E-3	0.97	90590	3.336	0.36	10998	2.06E-9
E-4 (1 h)	3999	2.81E-3	0.92	31223	1.047	0.51	16796	2.04E-9
E-1 (7 d)	2276	1.11E-3	0.80	13054	1.377	0.37	7254	1.52E-6
E-2 (7 d)	1873	2.44E-3	0.95	46968	4.88	0.35	3175	2.70E-6
E-3 (7 d)	2564	8.58E-3	1.00	48139	7.161	0.48	8085	2.40E-6
E-4 (7 d)	1672	2.64E-3	0.96	19587	9.390	0.45	1093	2.16E-6

Increasing the immersion time to 7.0 days decreased all the impedance parameters that support the occurrence of coating degradation compared to the same values obtained after 1.0 h immersion. This was clear especially for E-2, E-3, and E-4, which might be attributed to the presence of nonreacted epoxide groups remain in the system and the hydrolytic degradation can be responsible for the breakdown of etheric linkages causing electrolyte diffusion [45]. This indicates that corrosive chloride ions diffused into the coating/metal interface at a very short immersion time i.e. invasive penetration of the corrosive electrolytes [46].

4. CONCLUSIONS

Bisphenol A diglycidyl ether epoxy resin (DGEBA) was cured by polyamidoamine adducts (ARADUR PA450) in different stoichiometry variations to fabricate four DGEBA-PA450 epoxy coatings. The mechanical properties such as hardness, flexibility, cross-hatch, film thickness, gloss, and scratch resistance properties have been reported, irrespective of stoichiometry variations. The four DGEBA-PA450 epoxy coatings passed the mandrel bend test perfectly. Also, cross-hatch tests confirmed that all coatings had an excellent performance. The FTIR-ATR showed clear bands belong to the functional groups of the fabricated coatings. The corrosion behavior of the DGEBA-PA450 epoxy coatings was also investigated using EIS measurements after 1 hour and 7 days immersion in 3.5% NaCl solutions. The EIS data indicated that all samples showed consistency in corrosion resistance when the measurements were taken after 1 hour as a result of the high cross-linking density. Increasing the immersion time to 7 days led to a slight decrease in the corrosion resistance due perhaps to some degradation on the surface of the coatings under the influence of the corrosiveness action of the chloride ions. Results together showed clearly that all the fabricated DGEBA-PA450 coatings showed superior mechanical properties as well as excellent resistances against corrosion in 3.5% NaCl solutions.

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