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Mechanical Properties and Corrosion Behavior of Different Coatings Fabricated by Diglycidyl Ether of Bisphenol-A Epoxy Resin and Aradur®-3282 Curing Agent

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Fabrication of four blend samples of diglycidyl ether of bisphenol-A (DGEBA) epoxy resin cured by physical mixing with Aradur®-3282 polyamidoamine adducts (Aradur®-PA3282) as a curing agent at ambient temperature has been reported. The thermal degradation, mechanical properties and corrosion behavior of these fabricated DGEBA-PA3282 samples were investigated. Composition of coatings was confirmed using Fourier-transform infrared spectroscopy attenuated total reflectance (FT-IR-ATR). Scratch tester, mandrel bend, cross hatch tester, and pendulum hardness measurements were employed to report the mechanical properties of the different coatings. Corrosion tests were carried out for coated steel coupons after their immersion in 3.5 wt.% sodium chloride solutions for 1 h and 7 days. All fabricated coatings have excellent thermal and mechanical properties. Electrochemical impedance spectroscopy measurements indicated that the different DGEBA-PA3282 epoxy samples can be employed as protective coatings against corrosion in the freely aerated 3.5 wt.% NaCl solutions.

Keywords: Aradur®-3282 polyamidoamine adducts, bisphenol-A diglycidyl ether, corrosion resistance, mechanical properties, sodium chloride solution, thermal degradation

1. INTRODUCTION

A coat is a thin protective layer, typically 50-100 μm. It is well known that the use of coatings in the protection of metals and alloys is one of the most important methods and is considered as the first line defense against corrosion in aggressive media [1-7]. It is also know that coatings have specific engineering properties of a substrate metal and/or alloy by modifying or applying a thin layer at its surface [8-10]. Coatings are usually applied on surfaces where immersion is not continuous such as the external surfaces of tanks and pipes. The driving force for the advancement in the industry of coatings has been to improve the corrosion and wear resistances of the coating and the coated materials. 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 [11-13].

Corrosion protection by coatings can be provided by one or more of several mechanisms; these are [13-15]: (i) a barrier coating that prevents the corrosive environment from reaching the base metal (thick lining), (ii) an electrically resistive coating that slows down electrochemical corrosion reactions (organic coating), (iii) a noble metal coating that ensures that the base metal is in the passive state, (iv) an inhibitor coating that slows electrode reactions; and (v) a sacrificial metal coating that corrodes while giving cathodic protection to the base metal (galvanizing). Organic coatings as example are widely used in the protection of the metallic structures against corrosion due to their high barrier and superior mechanical properties [11-15].

Although there are many organic 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 [16]. There are many curing agents can be used for epoxy applications; of that polyamide, polyamine, and polyamidoamine are often employed. However, the performance of epoxy curing system is affected primarily by molecular weight of the epoxy resin as well as concentration of the curing agent [17]. Under some conditions, epoxy coatings can suffer surface abrasion and poor resistance to the initiation and propagation of cracks, which lead to the presence of some defects in the coatings that in turn impair their appearance and mechanical strength. These defects can also act as pathways accelerating the diffusion of water, oxygen, and corrosive species onto the metallic substrate, resulting in its localized corrosion [18,19]. It has been reported [20] that 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. For that it is very important for researchers to find the unique combination of curing agent and epoxy resin to obtain excellent mechanical properties and good corrosion resistances.

In our previous work [12], we reported the fabrication of various epoxy coatings with optimized quantity of polyamidoamine adducts ARADUR-PA450. In the current study, we investigated the fabrication, mechanical properties, and corrosion behavior of another set of blend samples of diglycidyl ether of bisphenol-A (DGEBA) epoxy resin with optimized quantities of Aradur®-PA3282 as a curing agent. The chemical composition of DGEBA-PA3282 coatings was confirmed using FTIR-ATR technique. The mechanical properties were also evaluated using scratch test, mandrel bend test, pendulum hardness, and cross hatch measurements. The electrochemical impedance spectroscopy investigations were used to study the corrosion behavior of the fabricated coatings after their immersions in freely aerated stagnant 3.5 wt.% NaCl solutions for short exposure period, 1 h and long immersion period, 7 days.

2. EXPERIMENTAL

2.1. Chemicals and materials

Polyamidoamine adducts ARADUR 3282 (hardener, PA-3282, Huntsman Advanced Materials) as a curing agent, bisphenol A diglycidyl ether epoxy resin (DGEBA, Hexion Chemicals), acetone (Merck, 99%), methyl isobutyl ketone (MIBK, Merck), and xylene (Merck, 99%). A 3.5 wt.% sodium chloride (NaCl, Merck, 99%) was prepared by dissolving an amount of 35 gm NaCl in 1 L doubly distilled water. Glass and steel plates were used as the coated substrates in order to perform the different characterization measurements.

2.2. Fabrication of the epoxy coatings

A series of epoxy coatings was fabricated by mixing up different percentages of DGEBA resin with various additives of PA-3282 as a hardener. This process includes the use of MIBK and xylene as organic solvents in the presence of an air releasing agent. A considerable amount of DGEBA resin was first stirred at 500 rpm in a dispermat mixer (BYK Gardener, Germany) for 5 min; to this the MIBK and xylene were gradually added at the same speed. The air releasing agent was added drop by drop during the initial mixing period to achieve homogeneous mixing with the organic solvents. The PA-3282 hardener was finally added to the aforementioned mixture and all components were stirred at 1000 rpm. The obtained coatings were then applied on different sizes of glass and steel plates to be employed in the different mechanical and electrochemical tests. The percentages of the chemical compositions for the produced DGEBA/PA-8232 coatings can be seen as shown in Table 1.

2.3. Fourier-transform infrared spectroscopy (FTIR-ATR) investigation

FTIR-ATR spectra were recorded for the fabricated coatings on a Perkin-Elmer infrared spectrophotometer 1720X equipped with a liquid nitrogen-cooled mercury-cadmium-telluride detector.

2.4. Thermal degradation analysis

A differential scanning calorimetry (DSC, Shimadzu DSC60) was used to thermally characterize the coatings under consideration. The following procedures were used to thermally characterize our fabricated coatings: (i) The pan and lid was placed on the microbalance and its mass was noted down; (ii) The sample was weighted separately and its mass was noted; (ii) Using tweezers, the sample was placed in the pan and the lid was placed on top; (iv) The pan with lid was placed in the sample press and the lever was pulled down; (v) By same procedure, the reference pan was prepared then placed in the auto sample tray; (vi) Both reference and sample pan weights were measured and recorded properly;(vii) The sample was placed on the DSC machine and started the run with definite cooling and heating parameter; and (viii) Once all the runs were completed, the set up was left on for half an hour.

2.5. Mechanical properties measurements

The gloss measurements for the different samples were performed using a tri-gloss meter, Sheen Instruments Co (UK). The gloss measurements were performed at 20° and 60° glass unit (UG). The thickness of the film applied on the surface of the glass and steel plates 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.

2.6. Corrosion behavior measurements

The steel substrates for electrochemical corrosion measurements were first ground using different sizes of emery papers and then rinsed with acetone. The substrates were then dried before the different epoxy coatings were applied on the steel panels using a film applicator. The coated samples were then left at room temperature to dry. 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), were used as the working, counter, and reference electrodes, 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. FTIR-ATR investigation

The chemical compositions for the different fabricated DGEBA-PA3282 coating formulations are shown in Table 1. The FTIR-ATR analysis was carried out on the surface of all fabricated samples to confirm the homogenious dispersion of the DGEBA epoxy coating with the Aradur®-PA3282 hardener at different stoichiometric variations (*see Table 1*) and to identify the functional groups of the molecules of the coatings. FTIR-ATR spectra shown in Fig. 1 were acquired for a dry surface of the different coating coupons after its application on glass substrates. The spectra were collected at a wavenumber range between 500 and 4000 cm^{-1} to see the reflectance for every spectrum appeared from the coated surfaces.

Table 1. Chemical compositions for the different fabricated DGEBA-PA3282 epoxy coatings.

Epoxy coating	Composition					
	PA-3282	MIBK	Air release	Xylene	DGEBA	Stoichiometry
ERC-1	19.98	20	0.2	20	Balance	+10.0
ERC-2	18.16	20	0.2	20	Balance	0.00
ERC-3	16.34	20	0.2	20	Balance	-10.0
ERC-4	14.53	20	0.2	20	Balance	-20.0

It is well known that Aradur®-3282 has a heterocyclic amine chemical structure that contains multi functional groups of -N=N-, $-NH_2$, -OH, =C=O, etc. Aradur®-3282 molecule is a substitute imidazole that may be used either as a latent catalytic curing agent for liquid epoxy resins or as a latent accelerator for anhydride and amine cured epoxy. Also, the chemical structure of DGEBA molecule [12] contains variety of organic groups such as aromatic rings, $-CH_3$, ≡C-O-C≡, etc. It is clearly seen from Fig. 1 that all FTIR spectra showed the same peaks at 827, 1038, 1118, 1181, 1238, 1392, 1459, 1508, 1606, 2361, 2853, 2923, and 3281 cm^{-1}. These bands are very close to the ones obtained at the same condition for the coatings recorded in our previous work [12] where, 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 [12,21-23]. Also, the C-H out-of-plane deformation vibration bands at 827 and 770-730 cm^{-1} are from the ring vibrations [22,23]. The broad band between 3200 and 3500 cm^{-1} is mainly due to the O-H stretching of hydroxyl groups might form due to the formation of DGEBA/PA3282 epoxy coating [22,23]. It is also seen from Fig. 1 that the increase of the stoichiometric variation (Table 1) increases the intensity of the transmittance of the coating. The FTIR-ATR spectra thus confirm that the mixing of DGEBA and PA-3282 with the reported stoichiometric variations could lead to the different fabricated coatings.

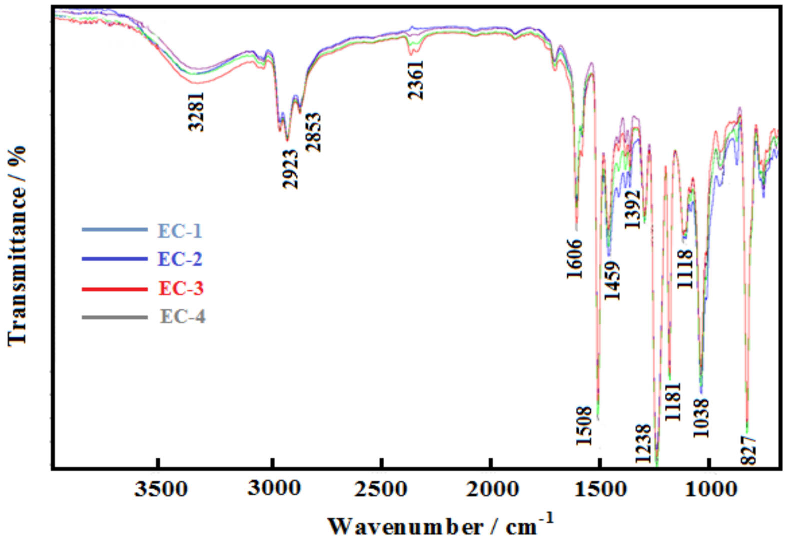

Figure 1. FTIR-ATR spectra obtained over a wavenumber range between 500 and 4000 cm^{-1} for the dry surfaces of the different fabricated DGEBA-PA3282 epoxy coatings.

3.2. Thermal degradation analysis

A differential scanning calorimetry (DSC) is a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference is measured as a function of temperature. Fig. 2 shows the recorded DSC versus temperature for the different fabricated DGEBA-PA3282 epoxy coatings. The DSC results showed that the main glass transition temperature (TG) for ECR-1 coating sample recorded 47.95 ºC. This value changed to 46.56 ºC and 49.42 ºC for ECR-2 and ECR-4 coated samples, respectively. The highest TG value was recorded for ECR-3 epoxy coating, 51.01 ºC. The high TG values for ECR-3 then ECR-4 compared to ECR-1 epoxy coating sample may be attributed to a better physical interaction between the polyamide (Aradur®-3282) hardener and the DGEBA epoxy resin moieties at the stoichiometric variations equivalent to ECR-3 and ECR-4.

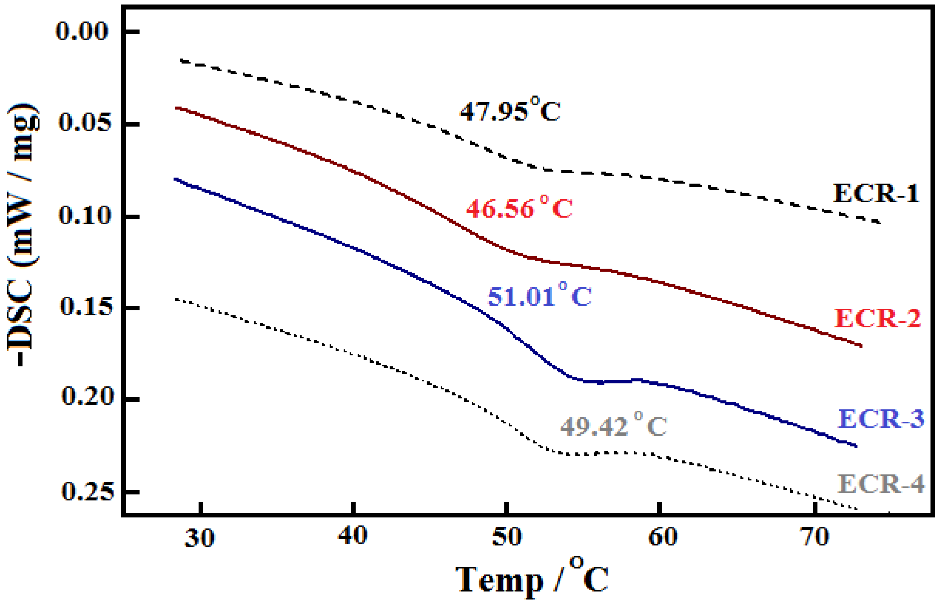

Figure 2. The variation of DSC (mW / mg) as a function of temperature (ºC) for the four fabricated DGEBA-PA3282 epoxy coatings.

3.3. Mechanical properties of the epoxy coatings

The dry film thickness, scratch resistance load, Koenig hardness, mandrel bend, cross hatch, and gloss measurements have been carried to investigate the role of Aradur®-3282 with the stoichiometric variations shown in Table 1 on the mechanical properties of the produced four DGEBA-PA3282 epoxy coatings. The values of dry film thickness, scratch resistance load, Koenig hardness, mandrel bend, cross hatch, and gloss measurements at 20º and 60º gloss unit (GU) obtained for the glass coated DGEBA-PA3282 samples are respectively listed in Table 2. The dry film thickness was measured on glass coated substrates to record an average value between 60 ~ 80 µm for our all fabricated coatings. The scratch resistant properties of the four fabricated epoxy coatings were measured on a dry film thickness of 60 ~ 80 µm that was applied on steel substrates and was left to completely dry. The scratch resistance recorded the highest value for ERC-2 flowed by ERC-1 and ERC-3 and the lowest value was obtained for ERC-4. According to Motawie et al. [24], the value of the scratch hardness increases due to the presence of polar hydroxyls and oxirane moieties in the backbone of the polymeric chain of the Aradur®-3282 curing agent.

The Koenig hardness for the four DGEBA-PA3282 coatings was determined on a dry film was applied on a glass substrate and having an average thickness of 60 ~ 80 µm. This layer thickness ensures that the influence of the substrate was negligible during the measurement of the Koenig hardness because a layer of at least 25 µm thicknesses is required to minimize the influence of the substrate as stated by the ASTM standards. The highest Koenig hardness value was recorded for ECR-3 coated coupon, while the lowest value was obtained for ECR-4 as can be seen from Table 2. Bhattacharya et al. [25] have stated for epoxy coating systems that the hardness value is directly related to the proportion of cross-linking between epoxide groups and curing agents. It is worth mentioning also that all the reported epoxy coatings passed the mandrel bend test perfectly. As well as, all samples had an excellent performance as indicated by the cross-hatch test. Table 2 shows also that the measured gloss values at 20º and 60º were consistent for all epoxy coatings. It has been reported [26] that a greater gloss value than 70 GU at 60° for coatings should be measured again at 20° because both 20° and 60° cover the majority of coatings applications.

Table 2. Koenig hardness, dry film thickness, scratch resistance load, mandrel bend, cross hatch, and gloss measurements for the different DGEBA-PA3282 epoxy coatings.

DGEBA -PA3282	Measuring test						
	Dry film thickness (µm)	Scratch resistance load at mar failure (kg)	Koenig hardness	Mandrel bend test	Cross hatch test	Gloss Measurement @	
						20° GU	60° GU
ERC-1	60 ~ 80	8.00	132	Pass	Excellent	95	94
ERC-2	60 ~ 80	8.50	131	Pass	Excellent	100	94
ERC-3	60 ~ 80	6.00	135	Pass	Excellent	101	96
ERC-4	60 ~ 80	5.50	124	Pass	Excellent	101	95

3.4. Electrochemical impedance spectroscopy (EIS) investigations

We have been successfully employing the EIS method to explain the corrosion mechanisms metals and alloys as well as their protection in different aggressive environments [27-41]. We also used the EIS technique to evaluate corrosion behavior of different coated metals in chloride solutions [2,4,6,12]. In this work, the EIS measurements were performed to determine kinetic parameters for electron transfer reactions at the interface of the coated steel coupons and the sodium chloride solution. EIS Nyquist plots obtained for (a) ERC-1, (b) ERC-2, (c) ERC-3, and (d) ERC-4 steel coupons respectively, after (1) 1.0 hour and (2) 7.0 days immersion in the aerated stagnant 3.5 wt.% NaCl solutions are shown in Fig. 3. These plots were fitted to the best equivalent circuit model as shown in

Fig. 4. The values of the parameters obtained by fitting the equivalent circuit shown in Fig. 4 are listed in Table 3.

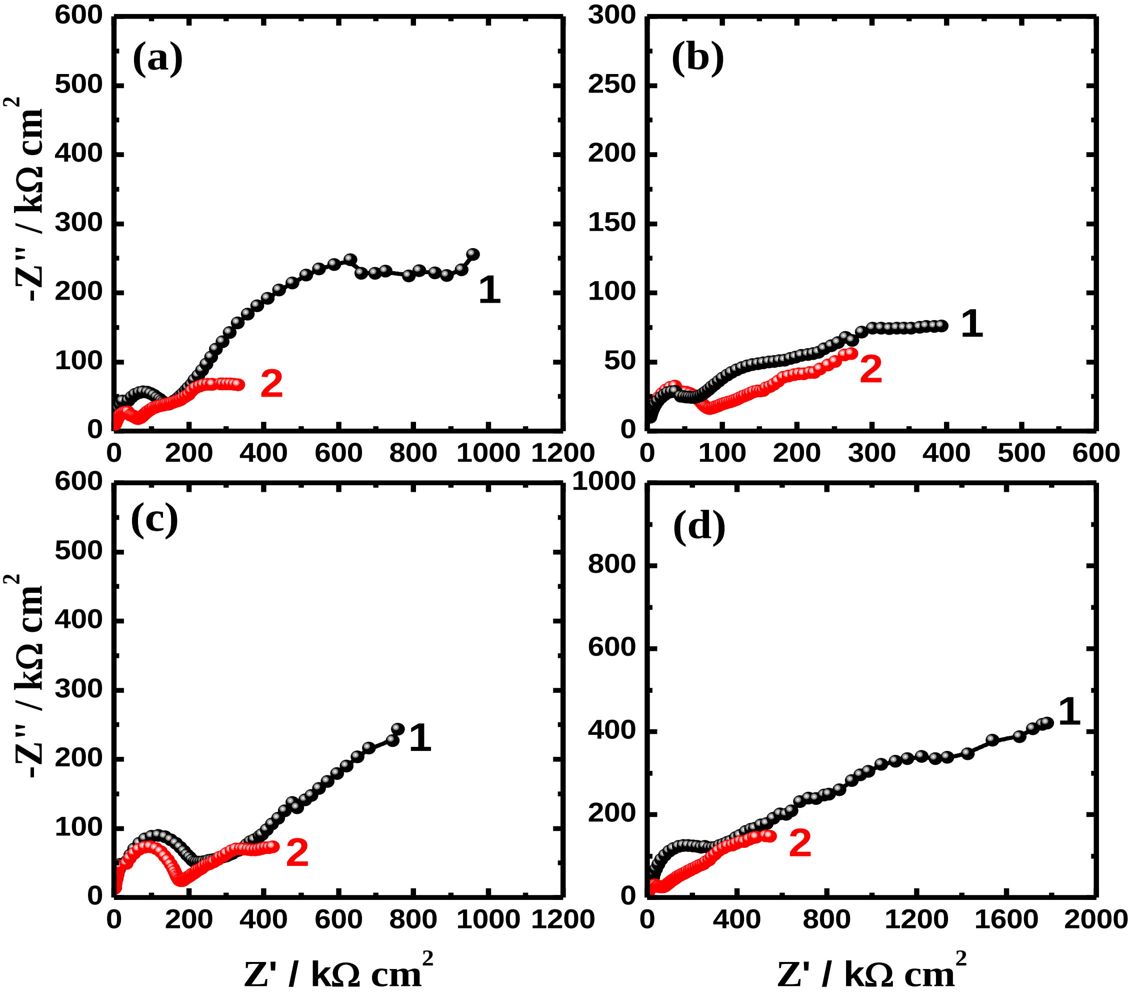

Figure 3. Typical Nyquist plots obtained for (a) ERC-1, (b) ERC-2, (c) ERC-3, and (d) ERC-4 steel coupons respectively, after (1) 1.0 hour and (2) 7.0 days immersion in the aerated stagnant 3.5 wt.% NaCl solution.

The symbol parameters of the equivalent circuit model shown on Fig. 4 can be defined according to the usual convention, where 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 shows that the Nyquist spectra for all the coated steel electrodes have only one single semicircle followed by a segment whether the immersion time was 1 hour or 7 days. It is well known that the bigger diameter of the obtained semicircle as well as the larger the segment the higher corrosion resistance. At this condition, the diameters of the semicircles at high frequency values can be considered as the charge transfer resistance and the semicircles at high frequencies are generally associated with the relaxation of electrical double layer capacitors [43-46].

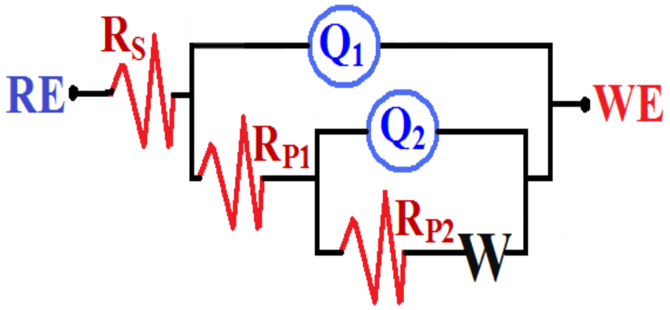

Figure 4. The equivalent circuit model used to fit the experimental data shown in Fig. 3.

It is seen from Fig. 3 that the diameters of the semicircle and the obtained segment are bigger over the short exposure period, i.e. 1 hour (curves 1). Increasing the immersion time to 7 days decreased the diameter of the semicircles as well as shortened the passivation segment. The corrosion behavior for all coated steel samples after 1 hour immersion in the chloride solution 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. It seems that increasing the immersion time to 7 days before measurement decreases the corrosion resistance for all coated steel coupons.

Table 3. EIS parameters obtained by fitting the Nyquist plots shown in Fig. 3 with the equivalent circuit shown in Fig. 5 for the epoxy coatings immersed in 3.5% NaCl solutions for 1 h and 7 days, respectively.

DGEBA-PA3282	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		
ERC-1 (1 h)	1475	2.95E-3	0.92	115.7	1.44	0.49	81.80	6.61E^{-6}
ERC-1 (7 d)	1437	3.33E-3	0.97	113.8	4.64	0.14	64.77	0.85E^{-6}
ERC-2 (1 h)	1598	2.22E-3	0.96	111.5	6.16	0.37	89.74	6.04 E^{-6}
ERC-2 (7 d)	1488	2.62E-3	0.99	110.7	3.30	0.15	73.95	0.39 E^{-6}
ERC-3 (1 h)	1693	1.85E-3	0.96	117.8	2.95	0.32	100.99	5.99 E^{-6}
ERC-3 (7 d)	1532	2.49E-3	0.98	114.6	4.22	0.17	81.83	0.51 E^{-6}
ERC-4 (1 h)	2227	1.68E-3	0.98	130.3	0.82	0.30	137.39	6.21 E^{-6}
ERC-4 (7 d)	2104	2.15E-3	0.95	126.3	2.93	0.18	95.50	0.54 E^{-6}

This is because the Nyquist spectra that were recorded after 7 days (Fig. 3, curves 2) showed smaller diameters for the obtained semicircles and shorter segments, which is most probably due to the degradation of coatings with increasing exposure time. According to Ramezanzadeh and Attar [47], the degradation of coatings may occur due 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. Liu et al. [48] have reported that the degradation of coatings can be resulted from the diffusion of the present corrosive chloride ions into the coating/metal interface at a very short immersion time and attack the metal surface causing its corrosion. It is seen from Table 3 that the values of R_S, R_{P1} and R_{P2} recorded higher values for all the epoxy coatings. The CPEs, Q_1 with its n values close to unity represent double layer capacitors.

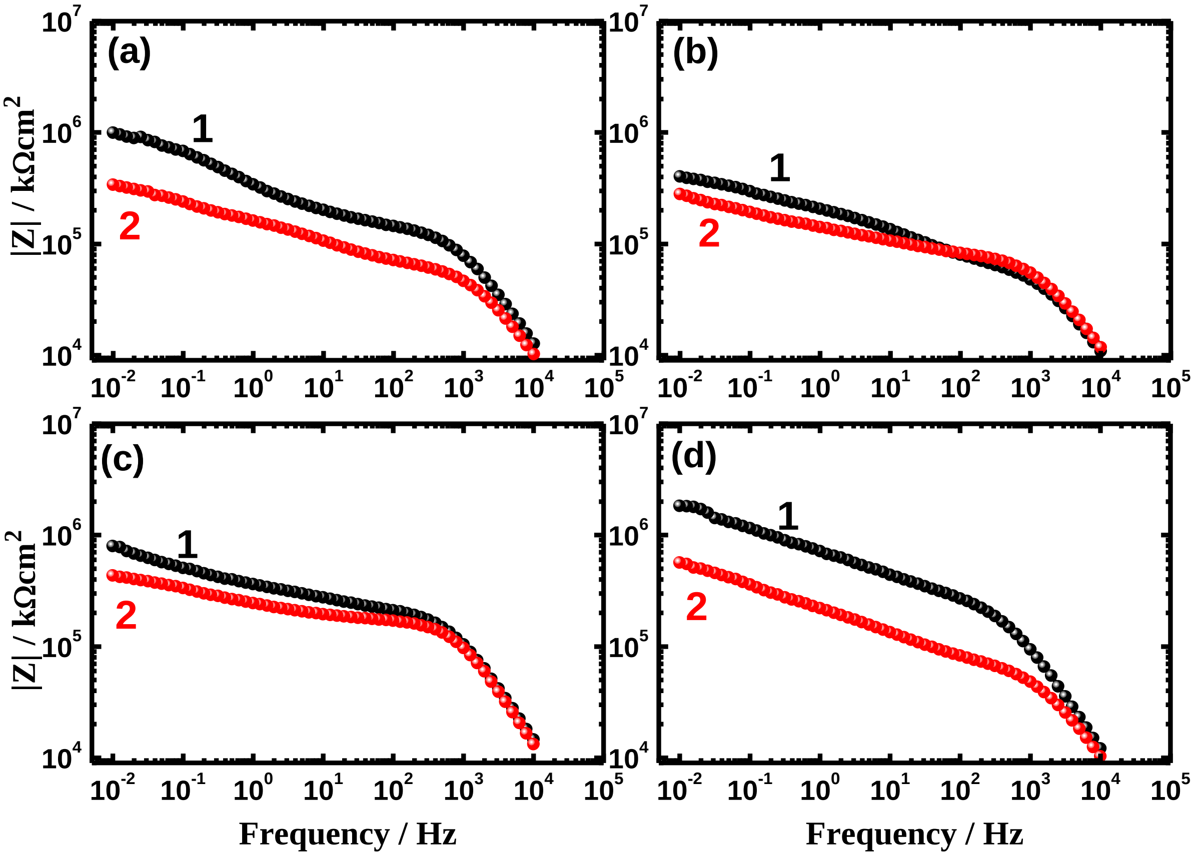

Figure 5. Bode impedance plots obtained for (a) ERC-1, (b) ERC-2, (c) ERC-3, and (d) ERC-4 coated steel coupons respectively, after (1) 1.0 hour and (2) 7.0 days immersion in the aerated stagnant 3.5 wt.% NaCl solution.

The CPEs, Q_2 with its n value varies between 0.18 and 0.49 represent Warburg (W) impedance [12]. It is also indicated by the presence of W in the equivalent circuit model that the degradation in the top coating layer due to the long immersion period, 7 days, does not occur by mass transfer. In order to confirm the data obtained from Nyquist plots and to better understand the effect of Aradur®-PA3282 additions on the corrosion resistance of DGEBA-PA3282 epoxy coatings, the Bode impedance plots for (a) ERC-1, (b) ERC-2, (c) ERC-3, and (d) ERC-4 coated steel coupons after (1) 1.0 hour and (2) 7.0 days immersion in the aerated stagnant 3.5 wt.% NaCl solution, respectively were obtained as shown in Fig. 5. It is clearly seen from Fig. 5 that all coatings showed high impedance (|Z|), particularly at low frequency region, which indicates on the passivation of the surface against corrosion [49-52]. Increasing the immersion time to 7 days decreased the impedance of the interface over all the frequency range and might be due to some degradation for coatings by the corrosive chloride ions present in the solution. Although, all the fabricated samples have high corrosion resistance but ECR-4 coating has the best performance. This agrees with the previous studies [12,17], which stated that the stability of epoxy resins in a corrosive environment was found to be increased when sub theoretical amount of polyamine is considerably lowered.

4. CONCLUSIONS

In this work, we reported the use of different additives of polyamidoamine adducts (Aradur®-PA3282) to cure bisphenol-A diglycidyl ether (DGEBA) epoxy resin to fabricate of four DGEBA-PA3282 coatings with different stoichiometric variations. Fourier-transform infrared spectroscopy, FT-IR-ATR, was used to confirm the composition of the fabricated epoxy coatings. The thermal degradation of the coatings was characterized using differential scanning calorimetry (DSC) method. The mechanical properties were studied using cross hatch tester, scratch tester, mandrel bend, and pendulum hardness measurements. Electrochemical impedance spectroscopy technique was used to characterize the corrosion resistance for the different samples after short, 1 h, and long, 7 d, exposure periods in aerated stagnant solutions of 3.5 wt.% NaCl. DSC investigation indicated that all coatings were thermally stable. Mechanical tests also indicated that DGEBA-PA3282 coatings have good mechanical properties. The corrosion measurements after 1 h immersion in the chloride test solution showed excellent corrosion resistance for the different coated coupons. While, after 7 d immersion the coupons suffered some degradation under the effect of the aggressiveness action of the chloride ions present in the test solution.

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