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The study on the influence of surface cleanness and water soluble salt on corrosion protection of epoxy resin coated carbon steel

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The corrosion resistance of epoxy-coated carbon steel was evaluated. The carbon steel surface was subjected to different treatment methods such as steel grit blasting and power tool treatment as well as contamination of water soluble salt. To study the effect of the surface treatments and contamination, the topology of the treated surface was observed by confocal microscopy and a pull-off adhesion test was conducted. The corrosion resistance of the epoxy-coated carbon steel was further examined by electrochemical impedance spectroscopy (EIS) combined with immersion test of 3.5 wt% of NaCl solution. Consequently, the surface contamination by sodium chloride with 16 mg/m^2, 48 mg/m^2 and 96 mg/m^2 didn't affect the adhesion strength for current epoxy coated carbon steel and blister and rust were not observed on the surface of epoxy coating contaminated by various concentration of sodium chloride after 20 weeks of immersion in 3.5 wt% NaCl aqueous solutions. In addition, the results of EIS test showed that the epoxy-coated carbon steel treated with steel grit blasting and power tool showed similar corrosion protection performance and surface cleanness such as Sa 3 and Sa 2.5 didn't affect the corrosion protectiveness of epoxy coated carbon steel.

Keywords : *EIS, epoxy, blasting, hygrothermal, blister*

1. Introduction

The mechanical surface treatment of metals is an important process and significantly affects the adhesion strength of coatings and adhesives. A number of studies have examined the effect of mechanical surface treatment on the strength and durability of adhesive joints using various adherents and adhesives.[1-7] Sancaktar and Gomatam reported that roughening the surface remove the weak surface layers and increase the reactivity of the surface, finally, led to the improvement of adhesion strength.[8] Shahid and Hashim reported that most surface treatments give rise to surface roughness and that, in general, the most effective treatment method to achieve the desired level of surface roughness and adhesion strength was grit blasting.[9] Grit blasting removes not only weak surface layers but also changes the chemical properties of the substrate.[7] However, the number of studies that relate surface roughness to the corrosion protection of epoxy-coated carbon steel under corrosive conditions is limited.

The presence of water-soluble contaminants at the metal/coating interface can accelerate corrosion process including osmotic blistering. The water-soluble salts, such as chloride, at the metal/coating interface accelerate osmotic blistering of the coating due to the chemical potential differences and penetrating electrolyte induces metallic corrosion. Both processes can lead to the deterioration of the coating system in a very short period of time followed by the loss of adhesion and coating breakdown.

The water soluble salt contamination and the amounts of allowable water soluble salts are very interesting research field and subjects of debate in the protective coatings industry. The experimental studies of maximum allowable chloride concentrations were reported by researchers.[10-18] Some researcher have reported the allowable chloride contamination is as low as 0.5μg cm^{-2}, whereas others the allowable chloride contamination is up to 127 μg cm^{-2}.[19] There are no established guidelines by industry so far because the effects of water-soluble contaminants at the metal/coating interface are significantly depending on generic type of coating and other parameters, such as coating thickness, pigments and additives.

The objective of the present work is to investigate the corrosion protectiveness of epoxy coating system by employing different surface treatments such as steel grit

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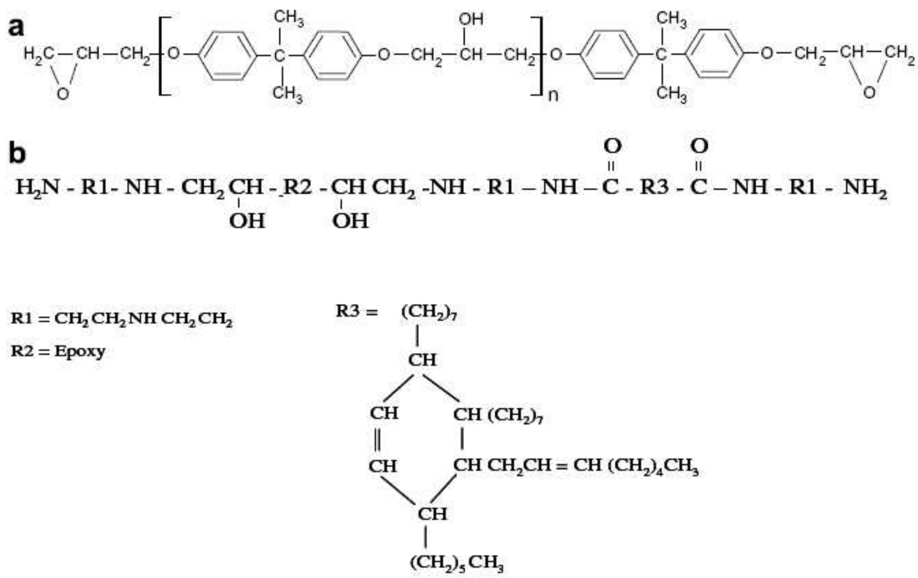


Fig. 1. Molecular structures of the epoxy coating system used in this study: (a) DEGBA, (b) PAEA.

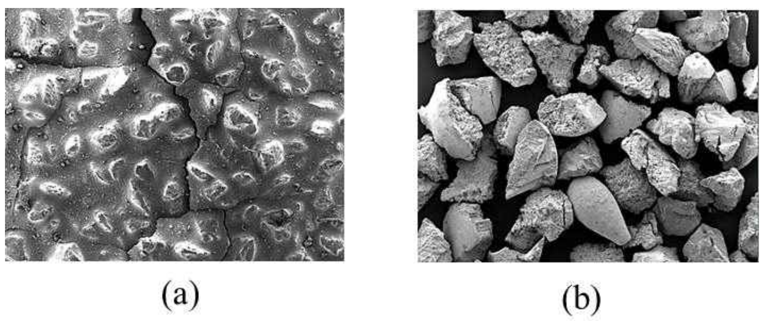


Fig. 2. SEM images of abrasives used in this study: (a) grinder wheel (power tool) and (b) steel grit.

blasting with different cleanness and power tool treatment. Also the effects of water soluble salts on corrosion protectiveness of epoxy coating system was examined in terms of different concentration of water soluble salts.

2. Experimental

2.1 Materials and specimen preparation

Bisphenol-A (DGEBA) and polyamide epoxy adduct (PAEA) based modified epoxy (KNA 340, IPK Korea) was used as the first and the second coatings onto the carbon steel. The molecular structures of epoxy resin and curing agents are shown in Fig. 1. The mixtures were vigorously stirred and degassed for 10min. Before coating, the surface of the carbon steel was treated by steel grit blasting and power tool. Then, the epoxy coating was coated on a carbon steel plate (150 × 70 × 3 mm) two times by airless spraying resulting in a final dry coating thickness of 320 ±10 μm, and then cured at 25 °C for 7 days.

2.2 Surface treatment and water soluble salt contamination

As mentioned above, the surface of the carbon steel was mechanically treated by different methods, including steel grit blasting and power tool treatment. Two surface cleanness of carbon steel surface, Sa 3 and Sa 2.5 (ISO 8501)[20] were achieved by steel grit blasting. After surface treatment, compressed dry air was blown across the surface to remove loose abrasive particles and dust, after which it was treated with acetone to remove any remaining oil or other contaminants. SEM photographs of the abrasive materials are shown in Fig. 2. Surface topology was analyzed by laser confocal 3D microscopy (Carlzeiss LSM 700, Germany) and the surface roughness was measured. Also, different concentration of sodium chloride was contaminated on the carbon steel before coating. The designed contents of sodium chloride (0.1 mg, 0.3 mg and 0.6 mg) were dissolved in each 10 ml of methanol. The each 1

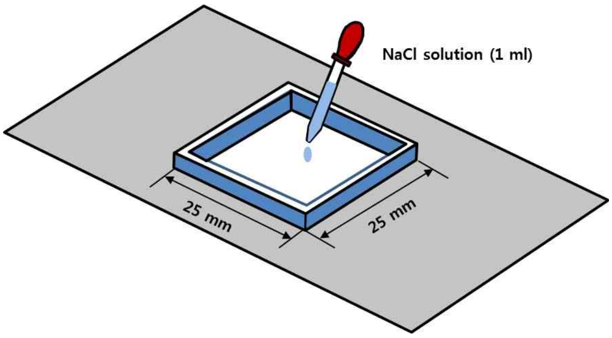


Fig. 3. Schematic diagram of Square dam for NaCl contamination test.

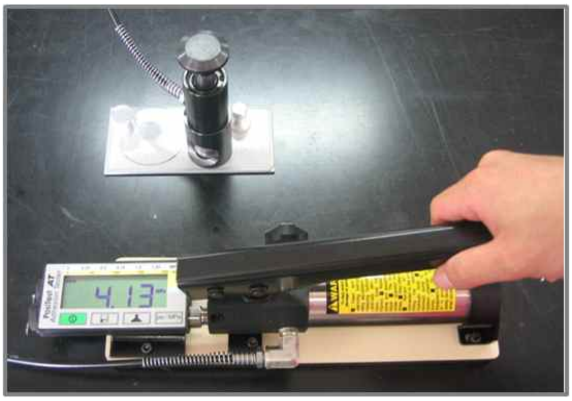


Fig. 4. Pull-off adhesion test equipment.

mg of sodium chloride solution were poured into square dam (25mm × 25mm), as shown in Fig 3, then, methanol was evaporated in convection oven with 40°C for 5 min. The theoretical concentrations of sodium chloride on carbon steel were 16, 48 and 96 mg/m^2, respectively.

For identification of the test specimens, the following terminology was adopted:

(1) G-Sa3: Steel grit blasting with Sa 3 cleanness
(2) G-Sa2.5: Steel grit blasting with Sa 2.5 cleanness
(3) PT: Power tool treatment
(4) G-16: Steel grit blasting (Sa 3 cleanness) contaminated by sodium chloride (16 mg/m^2)
(5) G-48: Steel grit blasting (Sa 3 cleanness) contaminated by sodium chloride (48 mg/m^2)
(6) G-96: Steel grit blasting (Sa 3 cleanness) contaminated by sodium chloride (96 mg/m^2)

2.2 Immersion test in sodium chloride solution.

The immersion test in 3.5 wt% of NaCl aqueous solution was conducted by the ISO 20340 standard method.[21] Epoxy-coated carbon steel panels (75×150×3 mm) subjected to different surface treatment and different concentrations of sodium chloride contamination were placed in the 3.5 wt% sodium chloride aqueous solution bath with 35°C. The total test periods were 20 weeks and the surface condition of the coated carbon steel panels was periodically inspected visually to detect any surface changes such as blistering and rust, etc.

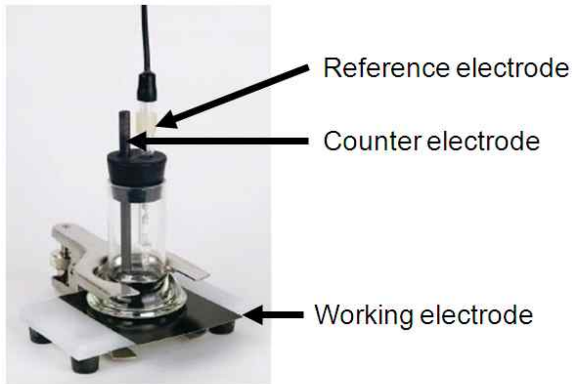


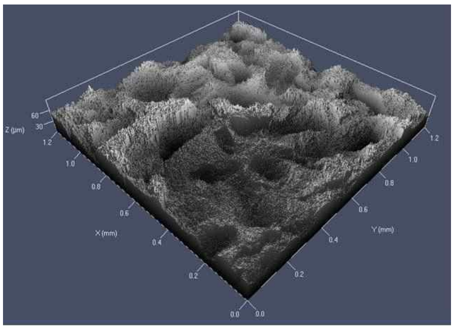
Fig. 5. Three-electrode electrochemical cell for EIS tests.

2.3 Adhesion properties

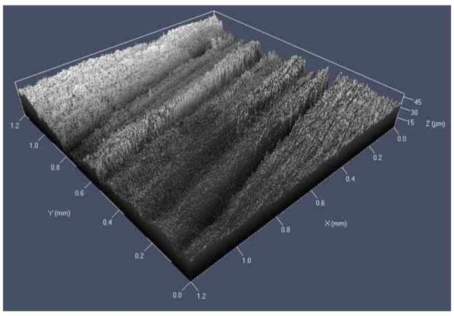
Following the surface treatment and sodium chloride contaminations, pull-off adhesion tests were performed to measure the adhesion strength of the epoxy coatings by the ASTM D 4541 standard method[22], as shown in Fig. 4. A dolly fixture 20 mm in diameter was glued to the surface of the coated specimens using an epoxy adhesive (Araldite 2011). After complete curing of the adhesive, the fixture was loaded by pull-off testing equipment (PA-0608, Defelsko Co) for the epoxy coated specimens after 20 weeks immersion in 3.5 wt% NaCl aqueous solution.

2.4 Electrochemical cell and Electrochemical Impedance Spectroscopy (EIS) combined with immersion test of 3.5 wt% NaCl solution

Immersion test in 3.5 wt% NaCl aqueous solution with 35°C was conducted to accelerate the cumulative effect of the electrolyte on the coating/carbon steel interface by the diffusion of the electrolyte into the coating. EIS was performed at the open circuit potential, using electrochemical impedance analyzer (SP-240, Biologics). The three-electrode electrochemical cell used to conduct EIS consisted of the epoxy-coated carbon steel as the working electrode (exposed area: 13.9 cm^2), a saturated calomel reference electrode, and a carbon counter electrode in 3.5 wt% NaCl solution (Fig. 5). Impedance values were obtained by applying a sine wave of 100 mV amplitude in a frequency range of 100 kHz to 100 mHz.



(a)



(b)

Fig. 6. Surface profile of carbon steel obtained by confocal microscopy: (a) Steel grit blasting and (b) power tool.

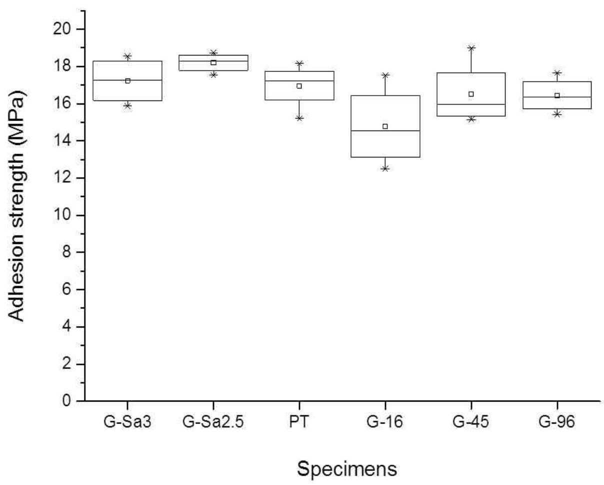


Fig. 7. Pull-off adhesion strength of the epoxy-coated carbon steel after 20 weeks of 3.5 wt% NaCl solution.

3. Results and Discussion

3.1 Surface analysis after surface treatment

The surface topology was observed after various surface treatments (Fig. 6). The surface roughness of carbon steel surfaces treated by steel grit blasting and power tools was measured by confocal 3D microscopy. The profile of the grit blasted surface was sharp and rough which can provide high degree of mechanical interlocking or "keying" within the coating system. On the other hand, the power tool treated surfaces showed not only a very sharp profile but also some directionality which is caused by the operation direction of the power tool. The average surface roughness of grit blasted surface was 11.6 μm which was approximately two times higher than that of the power tool treated surface (6.6 μm)

3.2 Effect of surface treatment methods and contamination on adhesion strength

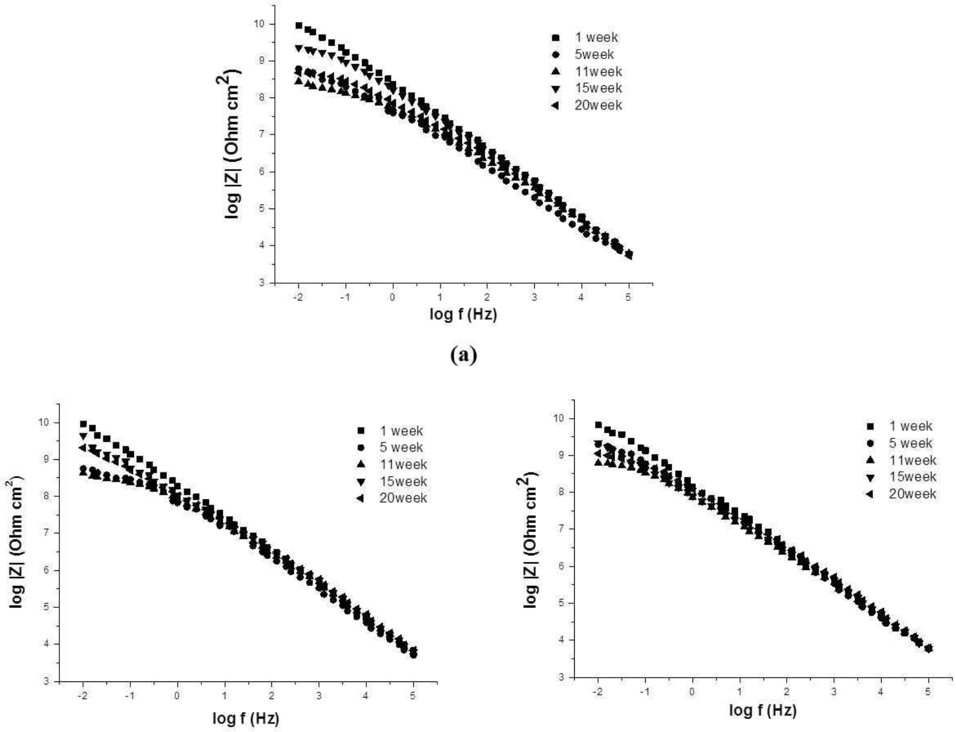
After 20 weeks of immersion in 3.5 wt% NaCl aqueous solution, pull-off adhesion tests was carried out for epoxy coated carbon steel specimens with different surface treatment (Steel grit blasting, and power tool) and various contents of sodium chloride contamination. As shown in Fig 7, the adhesion strength of the epoxy-coated carbon steel treated by steel grit blasting with different surface cleanness (Sa 3 and Sa 2.5) and power tool showed similar values resulting in higher 15 MPa. From the test results, it was clearly explained that the adhesion strength of power tool treatment was similar that of grit blasting treatment and the surface cleanness such as Sa 3 and Sa 2.5 didn't affect the adhesion strength for current epoxy coated carbon steel specimens.

The average adhesion strength of the epoxy-coated carbon steel contaminated by sodium chloride showed similar values resulting in higher than 14 MPa independent of sodium chloride concentration on the surface of carbon steel. From the results, it was clearly indicated that sodium chloride contamination of present study didn't affect the adhesion strength for current epoxy coated carbon steel specimens and these result was associated to the high osmotic blistering resistance of current epoxy coating system. In this study, any blistering and rust were not observed on the surface of epoxy coating after 20 weeks of immersion in 3.5 wt% NaCl aqueous solution.

3.4 Effects of surface treatment on corrosion protection as measured by EIS

The corrosion resistance of epoxy-coated steel with different surface treatments and surface contamination was examined by EIS combined with immersion test in 3.5 wt% NaCl aqueous solution.

Fig. 8 (a) shows the EIS Bode plot as a function of immersion time for epoxy coated carbon steel with Sa 3 grade of steel grit blasting. The impedance modulus of log |Z| at 0.01 Hz was slightly decreased from 8.91 × 10^9 Ω cm^2 to 2.69 × 10^8 Ω cm^2 after 11 weeks of immersion, after that, it slightly increased to 2.29 × 10^9 Ω



(b) (c)

Fig. 8. EIS spectra in Bode plot of epoxy-coated carbon steel with immersion test in 3.5 wt% NaCl solution: (a) G-Sa 3 (Steel grit blasting with Sa 3), (b) G-Sa 2.5(Steel grit blasting with Sa 2.5) and (c) PT (power tool treatment).

cm^2 after 15 weeks of immersion, then, decreased to $4.68 \times 10^8\ \Omega\ cm^2$ after 20 weeks of immersion.

Fig. 8 (b) shows the Bode plot as a function of the immersion time for epoxy coated carbon steel with Sa 2.5 grade of steel grit blasting. The decreasing trend of impedance modulus with respect to the immersion time was similar to that exhibited by epoxy coated carbon steel with Sa 3 grade of steel grit blasting. The impedance modulus of log |Z| at 0.01 Hz was slightly decreased from $9.96 \times 10^{9\ \Omega\ \mathrm{cm2}}$ to $4.17 \times 10^8\ \Omega\ cm^2$ after 11 weeks of immersion, after that, it also slightly increased to $4.47 \times 10^9\ \Omega\ cm^2$ after 15 weeks of immersion, then, decreased to $2.04 \times 10^9\ \Omega\ cm^2$ after 20 weeks of immersion.

Fig. 8 (c) shows the Bode plot as a function of the immersion time for epoxy coated carbon steel with power tool treatment. The decreasing trend of impedance modulus with respect to the immersion time was also similar to those exhibited by epoxy coated carbon steel with Sa 3 and Sa 2.5 grade of steel grit blasting. The impedance modulus of log |Z| at 0.01 Hz was slightly decreased from $6.46 \times 10^9\ \Omega\ cm^2$ to $6.03 \times 10^8\ \Omega\ cm^2$ after 11 weeks of immersion, after that, it slightly increased to $2.14 \times 10^9\ \Omega\ cm^2$ after 11 weeks of immersion then decreased to $1.10 \times 10^9\ \Omega\ cm^2$ after 20 weeks of immersion.

From the results of EIS measurement, it was clearly demonstrated that the corrosion phenomenon of epoxy coated carbon steel was not observed and slightly decreasing of impedance modulus after 11 weeks might be decreasing of pore resistance of epoxy coating because of penetrating of electrolyte into the pin holes or micro pores of coating. Additional increasing of impedance was considered to be blocking the pin holes or micro pores by corrosion products from carbon steel.[23)]

Fig. 9 (a) shows the Bode plot as a function of the immersion time for epoxy coated carbon steel with NaCl contamination of 16 mg/m^2. The impedance modulus of log |Z| at 0.01 Hz was slightly decreased from $6.29 \times 10^9\ \Omega\ cm^2$ to $2.24 \times 10^9\ \Omega\ cm^2$ after 20 weeks of immersion.

Fig. 9 (b) shows the Bode plot as a function of the immersion time for epoxy coated carbon steel with NaCl contamination of 48 mg/m^2. The impedance modulus of log |Z| at 0.01 Hz was decreased from $1.91 \times 10^{10}\ \Omega\ cm^2$ to $6.17 \times 10^8\ \Omega\ cm^2$ after 11 weeks of immersion, and then increased to $2.34 \times 10^9\ \Omega\ cm^2$ after 20 weeks of immersion.

Fig. 9 (c) shows the Bode plot as a function of the immersion time for epoxy coated carbon steel with NaCl

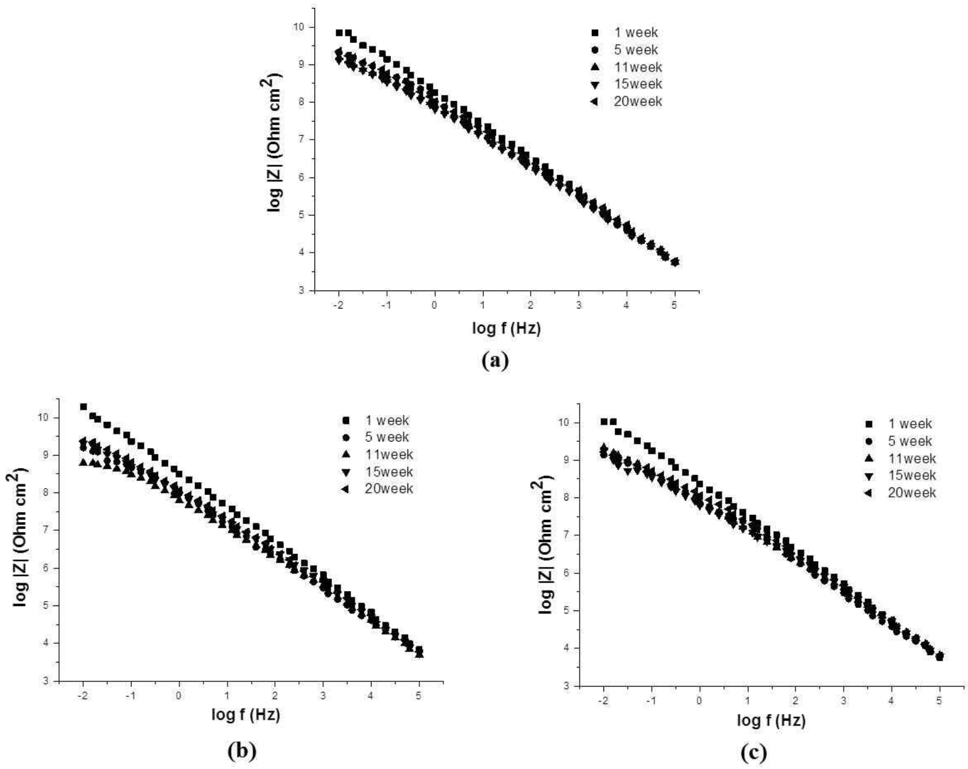


Fig. 9. EIS spectra in Bode plot of epoxy-coated carbon steel with immersion test in 3.5 wt% NaCl solution: (a) G-16 (Contaminated by NaCl (16 mg/m^2)), (b) G-48(Contaminated by NaCl (48 mg/m^2)) and (c) G-96 (Contaminated by NaCl (96 mg/m^2)).

contamination of 96 mg/m^2. The impedance modulus of log |Z| at 0.01 Hz was decreased from 1.05×10^{10} Ω cm^2 to 1.62×10^9 Ω cm^2 after 20 weeks of immersion. The slightly decreasing of impedance modulus was observed after 5 weeks independent of NaCl concentration and it seems not caused by NaCl contamination but by the penetration of electrolyte into the coating.

From the results of EIS measurement, it was clearly indicated that the effects of NaCl contamination on carbon steel on corrosion protection of epoxy coating was negligible under the concentration of NaCl and coating system in this study.

4. Conclusions

The conclusions drawn from this work are as follows:

1. A sharp and high-roughness carbon steel surface was achieved by steel grit blasting and power tool.
2. The surface cleanness such as Sa 3 and Sa 2.5 didn't affect the adhesion strength for current epoxy coated carbon steel.
3. In surface treatment such as steel grit blasting with Sa 3 and Sa 2.5 cleanness, and power tool, the corrosion of epoxy coated carbon steel was not occurred and surface cleanness such as Sa 3 and Sa 2.5 didn't affect the corrosion protectiveness of epoxy coated carbon steel.
4. The surface contamination by sodium chloride with 16 mg/m^2, 48 mg/m^2 and 96 mg/m^2 didn't affect the adhesion strength for current epoxy coated carbon steel.
5. Blister and rust were not observed on the surface of epoxy coating contaminated by sodium chloride with 16 mg/m^2, 48 mg/m^2 and 96 mg/m^2 after 20 weeks of immersion in 3.5 wt% NaCl aqueous solutions. Accordingly, the NaCl contamination on carbon steel in this study didn't affect the corrosion protectiveness of epoxy coated carbon steel.

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