

Short Communication

Electrochemical Impedance Spectroscopy Investigation of a Polyurethane Coating on Bridge 16Mnq Steel Surface

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Received: 28 December 2016 / *Accepted:* 11 February 2017 / *Published:* 12 March 2017

The bridge 16Mnq steel sample was successfully coated with polyurethane film in order to enhance its corrosion resistance. The electrochemical properties of polyurethane film coated samples with different coating thicknesses (60, 80 and 100 μm) were investigated using electrochemical impedance spectroscopy (EIS). Corrosion tests were carried out by exposing the coated system to NaCl aqueous solution with the concentration of 3.0% in a horizontal flat-cell. The improvement of corrosion resistance of the coated substrate was evaluated by the time dependent impedance parameters. The degradation phenomenon demonstrated by EIS measurements was related with the changes of mechanical properties of coated metals which could be measured by tests of microhardness and pull-off adhesion. Polyurethane coating was affirmed to possess strong adhesion and enhanced anticorrosion protection characteristics.

Keywords: Electrochemical impedance spectroscopy; Corrosion; Polyurethane; Pull-off adhesion; Microhardness

1. INTRODUCTION

Reinforced concrete is considered to be most versatile and economic structural material with excellent performance and long lifetime. Nevertheless, the corrosion of reinforcing steel seriously affects the long term performance of as-built structure, leading to security problem and economic loss. The concrete becomes passive owing to the formation of a protective oxide layer with the thick of about 10 nm after the insertion of carbon steel (C-steel). The newly generated layer is highly stable in alkaline environment with pH around 12.5. However, the corrosion problem still remained for concrete rebars due to the existence of aggressive species such as chloride ions and carbon dioxide in the concrete. Generally, carbonation causes uniform depassivation of the concrete while chlorides cause localized pitting corrosion. In order to minimize the damages of reinforced concrete structures by

corrosion, stainless steel rebars has been employed as an economical solution [1]. Stainless steel has been confirmed to have higher corrosion resistance than ordinary C-steel [2, 3]. In addition, the corrosion resistance performance of stainless steel rebars was better in comparison with that of investigated galvanized rebars [4]. However, detailed quantification on the improvement of corrosion resistance after the employment of stainless steel rebars was still not available.

Electrochemical impedance spectroscopy (EIS) has been considered as a non-destructive method for investigating the corrosion performance of coated metals that are exposed to water environment [5, 6]. Organic coatings play an important role in the effective protection of metals due to their function as physical barrier between metal surface and corrosive environment [7-10]. Nevertheless, a great deal of potentially corrosive species including ions, water and oxygen can penetrate almost all polymers [11-14]. Furthermore the penetrated water molecules can weaken the adhesion between metal and organic coating, leading to the corrosion of metal underneath film. Moreover, the corrosion resistant performance of painted system is determined by the nature of intermediate layer and metallic substrate [15, 16]. The impedance response of coated metals demonstrates significant change during the penetration process of corrosive species. Therefore, relevant information about corrosion process can be acquired by analysing the obtained EIS spectra.

EIS has demonstrated to be successfully applied for investigating the corrosion performance of carbon or galvanized steel substrates that are coated with diverse polymers such as epoxy-polyamide [17-19], alkyd [20] and polyester [21, 22] polymeric films upon the exposure to aqueous solution under ambient condition. The characteristic breakdown frequencies [23-25] and relevant impedance parameters using the equivalent electric circuits [26-28] method can be determined from the measured spectra. Then the impedance parameters in function of time can be further obtained, which is greatly important to evaluating the anticorrosive performance of coated systems. More recently, by comparing the impedance parameters of polyester coated galvanized steel substrate and pure galvanized steel substrate that were exposed to electrolyte solution, the adhesion degree between polyester and metal substrate could be related with various exposure conditions [16].

In this study, polyurethane resin was chosen to modify bridge 16Mnq steel owing to its excellent adhesion and hardness. Then electrochemical impedance spectroscopy (EIS), microhardness tests and pull-off adhesion tests were employed for investigating the degradation of coated metal system after being exposed to naturally aerated test electrolyte, leading to the achievement of relevant correlations between electrochemical performance and structural characteristics. In addition, the influence of adhesion degree between polyurethane and bridge 16Mnq steel on the corrosion resistance performance of coated metal system was evaluated.

2. EXPERIMENTS

The surface of bridge 16Mnq steel substrate (the composition of the investigated steel has shown in Table 1) was fabricated with a layer of two-component epoxy-polyamide film. The acrylic resin cured with aliphatic polyurethane was purchased from Sigma Coatings. Commercialized hot-dip galvanized panels for constructing overhead electrical transmission-line towers were degreased with

acetone, washed with distilled water and drip-dried before use. A polyurethane lacquer was formed by mixing a polyacryl based resin (MS-Clear 923-155) with an isocyanate based hardener (HS-Topcoat Hardener 929-93) at 2:1 ratio. The coating thickness was around 60-100 μm and was set by a barcoater. Curing of the coating took place in ambient atmosphere for 4 days.

Table 1. Chemical composition of the 16Mnq steel

Brand	C	Si	Mn	P	S	Alt
16Mnq	≤ 0.18	≤ 0.50	1.20~1.60	≤ 0.035	≤ 0.035	≥ 0.020

Electrochemical impedance spectra (EIS) were performed on a computer-controlled potentiostat (EG&G Model 283A) accompanied with lock-in amplifier (EG&G Model 5210). The coated metallic sample was connected to two different sacrificial anodes (aluminium and magnesium anodes) and the applied polarisation potentials were -1.0 V and -1.5 V (SCE), respectively [15]. Impedance measurements were carried out under ambient condition ($\sim 20^\circ\text{C}$) and the specific experimental parameters are set as follows: 40 kHz-1 mHz as frequency range and 15 mV as the sine wave superimposed to the applied potential. Five points per decade were collected and averaged over four cycles at each frequency. The *ZsimpWin 2.00* software was used for acquiring and analysing impedance spectra. Bode plots that is logarithm of the impedance modulus $|Z|$ and phase angle Φ in function of logarithm of frequency f can be presented with the obtained data.

For pull-off adhesion tests, the initial adhesion and the adhesion retained after immersion in 0.5 M NaCl aqueous solution were measured using a direct pull-off adhesion test. In this method, the test dolly was bonded to the coating using an appropriate adhesive. The samples for retained adhesion studies were removed from the solution at the end of the immersion test, rinsed thoroughly with distilled water and allowed to dry for 48 h at ambient temperature. A digital adhesion tester with a maximum applied load of 150 kg/cm was used.

An ultrahardness tester (MHT-4, Anton Parr, Austria) equipped with a knoop indenter was used to evaluate the hardness of the coatings. The hardness values were calculated by measuring the diagonal length of indentation.

3. RESULTS AND DISCUSSION

The impedance spectra of coated samples treated in 3.0% NaCl solution for different immersion times were measured. Fig. 1, Fig. 2 and Fig. 3 displayed the impedance spectra of coated samples with the thickness of 60 μm , 80 μm and 100 μm , respectively. Both Nyquist and Bode plots were given. The electrochemical performance of the polyurethane coated metals was greatly influenced by the exposure time. In the first few exposure hours, the impedance diagram exhibited phase shift of 90° over wide frequencies as an indicator of highly capacitive and the phenomenon was special for the metals modified with thickest film. Subsequently, the shape of diagram changed to two capacitive semicircles as the elapse of time, and the two semicircles could be attributed to the electric

properties of organic coating and faradaic process at the substrate, respectively. As for the samples coated with thinnest polyurethane films, the appearance of two capacitive semicircles is most prominently and could be observed at early exposure times. The impedance values exhibited a decrease for all tested specimens during the first hours of test. As to the specimens coated with polyurethane films of 60 and 80 μm thick, the initial decay for the impedance value was rather slow, and then the impedance values exhibited a new increase after 300 h exposure. Conversely, a continuous decrease in the impedance values for the thinnest film is observed at all times. Degradation of the coated specimens was first investigated by means of the break-point frequency method proposed by Haruyama et al. [29]. In this method, the values of a characteristic breakdown frequency f_b are determined experimentally from the impedance spectra, as they are related to the delaminated area in the initial stages of delamination. This characteristic breakdown frequency f_b is the frequency at which the phase angle $\varphi=45^\circ$ in the capacitive-resistive transition region.

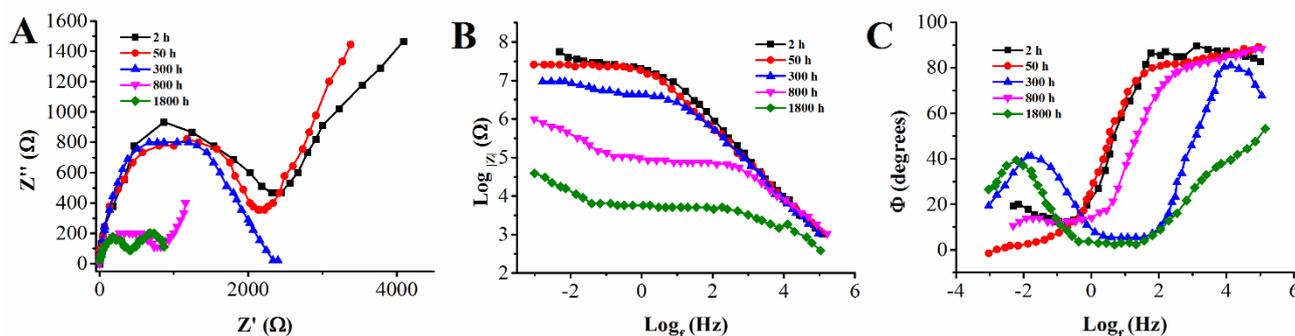


Figure 1. Experimental impedance diagrams of galvanized steel coated by polyurethane film with the thickness of 60 μm after the immersion process in NaCl solution for 2, 50, 300, 800 and 1800 h, respectively.

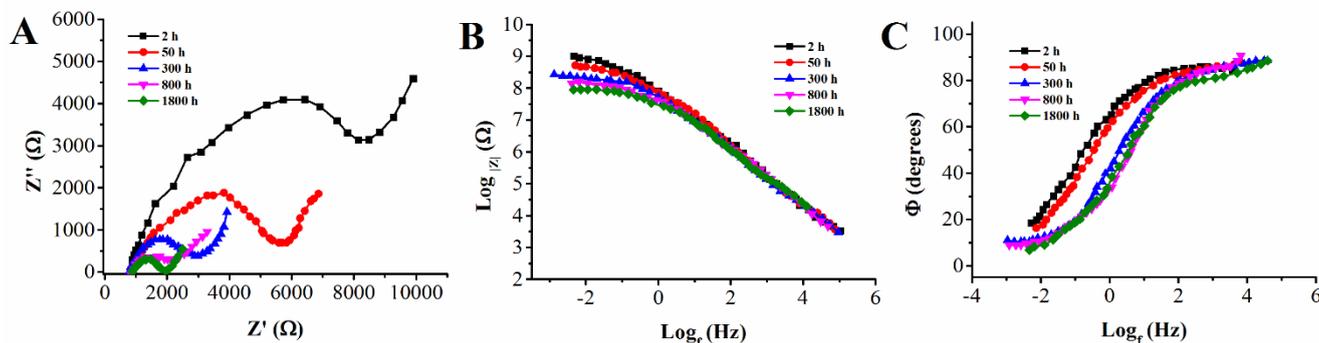


Figure 2. Experimental impedance diagrams of galvanized steel coated by polyurethane film with the thickness of 80 μm after the immersion process in NaCl solution for 2, 50, 300, 800 and 1800 h, respectively.

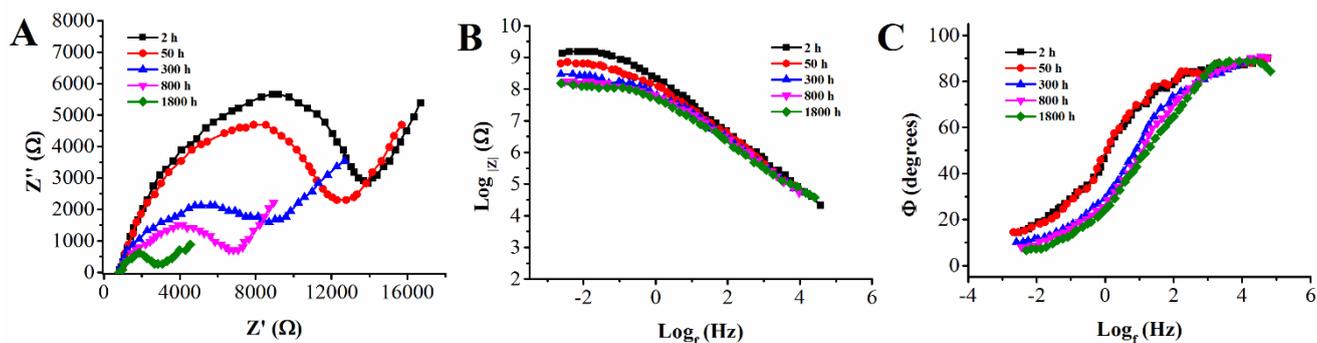


Figure 3. Experimental impedance diagrams of galvanized steel coated by polyurethane film with the thickness of 100 μm after the immersion process in NaCl solution for 2, 50, 300, 800 and 1800 h, respectively.

In the proposed method, the values of a characteristic breakdown frequency f_b related to the phase angle of 45° in the capacitive-resistive transition region could be determined experimentally by calculating the delaminated area in the initial stages of delamination as displayed in impedance spectra.

For the galvanized steel coated by polyurethane film with different thickness, a purely capacitive behaviour was observed, which might be resulted from the effective barrier film. The value of low-frequency limit for impedance modulus was higher than $10^9 \Omega \text{ cm}^2$ and the phase angle remained close to 90° for almost all tested frequencies. Therefore, one time constant that accounted for barrier of organic coating could be obtained from impedance spectra. Fig. 4A showed the simple equivalent circuit of the above-mentioned electrochemical behaviour, and the circuit was composed of resistive component (R_{PO}) and dielectric capacitor (C_C) in the parallel combination mode. The value of R_{PO} was larger than $10^8 \Omega \text{ cm}^2$, indicating the successful possession of barrier properties for as-prepared polymeric film. As expected the polymer could be easily lifted off, but the applied force was nearby the detection limit of the applied equipment [30]. In general all peel-off forces are reduced after exposure in humid air due to water replacing secondary polymer/iron oxide interactions [31]. In addition, the metallic substrate could be effectively isolated from aggressive environment as verified by the high enough R_{PO} value. However, as can be seen from the Bode phase diagrams, a small part of the frequency range exhibited capacitive behavior over time. The above phenomenon was more obvious for the film coated on carbon steel. Meanwhile, the values of impedance modulus showed a decrease to the new range of 10^6 - $10^8 \Omega \text{ cm}^2$. It can be concluded that polymeric film was an imperfect dielectric as indicated by the high frequency data.

At longer exposure time, a second time constant was eventually observed in the impedance diagrams, which was in the form as semicircle at lower frequencies in tested Nyquist diagrams. It was worth noting that partial area of the coated film as barrier was lost at the above-stage of degradation process, leading to the direct contact of underlying metal with aqueous environment. Therefore, in contrast to the first semicircle as an indicator of barrier characteristics of the organic coating, the second semicircle was an indicator of corrosion process occurring at the defective areas generated between the interface of coating and substrate. Particularly, the charge transfer from metal to the solution can be described by the second semicircle. Fig. 4B showed the equivalent circuit for

describing the impedance spectra of polymer film coated metal with defect. In this model, capacitor C_{DL} is a new parameter that represents the distribution of ionic charges on unprotected metallic substrate. In addition, resistive element, R_t , is a new parameter that is inversely proportional to the corrosion rate of metal.

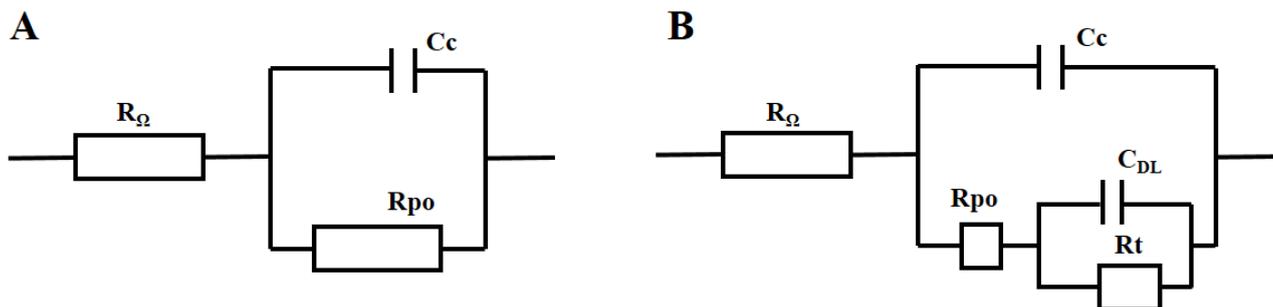


Figure 4. Equivalent circuits of (A) barrier coating system with one time constant, and (B) non-barrier coating system with two time constants.

As shown from Bode-phase diagrams measured with exposure time longer than 1500 h, the marked smaller impedance values were observed in the overall frequency range, indicating the occurrence of corrosion blisters that would lead to the damage of the polymer coating. With the beginning of the formation of blisters at the interface of metal and coating, the metal samples are no longer protected from corrosion effectively, as displayed by the smaller impedance values ($<10^6 \Omega \text{ cm}^2$) and higher breakdown frequencies ($>10^2 \text{ Hz}$). The obtained impedance spectra were analyzed with the relevant equivalent circuits shown in Fig. 4 and the parameters R_{PO} and C_C could then be determined. Fig. 5 showed the plots displaying the parameters such as R_{PO} and C_C in function of the exposure time in solution for the tested three systems. In addition, the break-point frequency values at phase angle $\phi = 45^\circ$ that can be obtained from impedance spectra are employed for evaluating the performance of metal/coating systems as well [32]. It can be confirmed that an increase of the polar surface energy component has a positive effect on the adhesion strength for polymer films with polar functional groups [33, 34]. It is worth noting that the capacitive-resistive transition was greatly related with the breakdown frequency. Moreover, the value of breakdown frequency could be determined from the delaminated area in the initial stage of delamination and the specific equation was shown as follows [29, 35]:

$$f_b = \frac{A_d}{2\pi\xi\xi_0\rho_0A} = \frac{KA_d}{A}$$

where A_d and A is the delaminated area and total area, respectively, ε is the dielectric constant of the organic coating, ε_0 is the vacuum permittivity and ρ_0 is the specific resistivity of organic coating in the delaminated area. Fig. 5C showed the values of the breakpoint frequencies in function of exposure time for tested three systems.

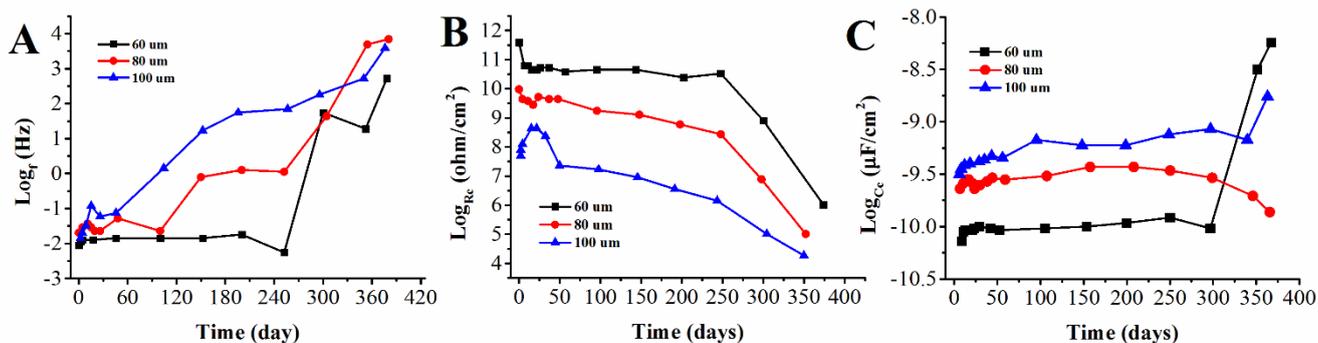


Figure 5. The impedance parameters including (A) coating capacitance C_C , (B) pore resistance R_{PO} and (C) breakdown frequency f_b in function of time.

The pull-off tests was also measured to investigate the adhesion between organic coatings and metal substrate. The obtained forces that required for the detachment of test dollies glued to coating from underlying metal can be employed to investigate the adhesion quantitatively. Both fresh sample and the sample after the electrochemical tests were observed. Table 2 showed the adhesion values calculated from pull-off tests. The adhesion between polyurethane coating and carbon steel was observed to be much stronger than that between polyurethane coating and galvanized steel. Furthermore, the forces required to detach the film from samples showed a decrease after the exposure of sample in the electrolyte solution. In addition, the decrease was much more significant for the galvanized steel painted samples than carbon steel painted samples.

Table 2. Pull-off test results.

Sample characteristic	No exposure	After exposure
60 μm thick coating	67.3	65.4
80 μm thick coating	30.2	29.1
100 μm thick coating	34.4	33.2

The change of mechanical parameters including plastic component (HU_{pl}), Martens microhardness (HM) and indentation modulus (EIT) after the electrochemical tests of coated samples were investigated as well. The loading/unloading curves displaying indentation depth in function of load was obtained for bridge Mnq 16 steel coated with polyurethane film at different thickness and the results were shown in Fig. 6. It should be noting that each point was determined using the average of same test 5 times that performed at 5 points on the surface of material. In all cases the mechanical behaviour of ploymer film was in similarity with that of plastic material. The maximum load that could be applied for the film-coated samples was 10 mN since the slope of corresponding plots would be changed with higher loads owing to the effect of metallic substrate on measured hardness of samples.

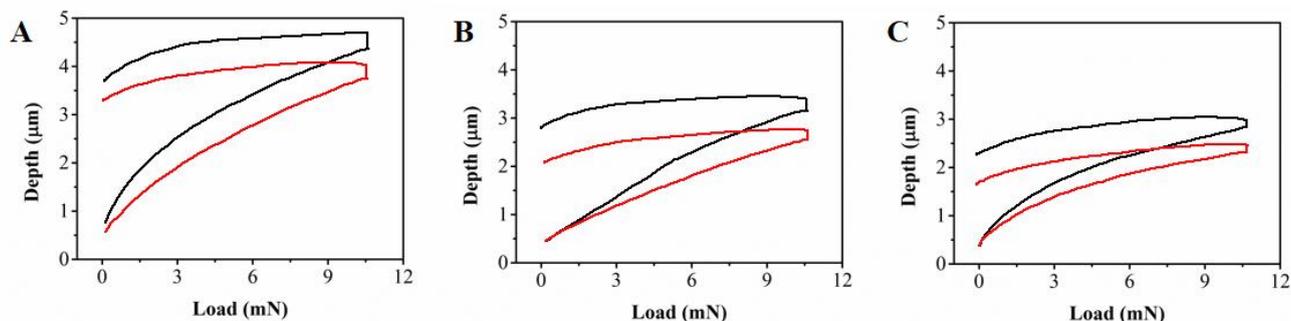


Figure 6. Curves of hardness versus load for the bridge Mnq 16 steel coated with polyurethane film with the thickness of (A) 60 μm , (B) 80 μm and (C) 100 μm prior and after exposure in 0.5 M NaCl solution for three month.

4. CONCLUSIONS

In conclusion, the surface of bridge 16Mnq steel substrate was successfully coated with polyurethane film in order to enhance the corrosion resistance of steel. The electrochemical properties of as-prepared samples can be evaluated by the time dependent impedance parameters obtained using the generalized equivalent circuit. The polyurethane film is found to provide a less effective protection to underlying metal with the decrease of coating resistance and increase of coating capacitance. Pull-off tests was employed to investigate the adhesion of organic coatings to metallic substrates. It was observed that polyurethane coating adheres more strongly on carbon steel than galvanized steel. In addition, the protection for bridge Mnq 16 steel was enhanced with the thicker polyurethane film.

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