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Electrochemical Impedance Spectroscopy Evaluation of Corrosion Protection of X65 Carbon Steel by Halloysite Nanotube-Filled Epoxy Composite Coatings in 3.5% NaCl Solution

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Corrosion by seawater is an electrochemical Corrosion, and all types of metals or alloys when they are in contact with seawater have a specific corrosion potential at a certain level of seawater alkalinity or acidity. Metal corrosion is a major technical problem and plenty of methods have been developed to provide solution. Inhibitor-enhanced coating can be recognized as the most efficient method. In this research, Halloysite nanotube (HNT) was used to create HNT-epoxy composite as protection towards corrosion without the inhibitor. The electrochemical impedance spectroscopy (EIS) study was done on HNT-epoxy composite coatings for corrosion protection carbon steel in 3.5% NaCl solution. The morphology analysis of the HNT was done by optical microscope and field emission scanning electron microscope(FESEM). The EIS characterizations showed a turning point of the composite coating from good to poor corrosion resistance performance. According to EIS measurements, increasing the halloysite concentration had resulted in the enhancement of the barrier effect and an increase in the ability to protect corrosion coating in NaCl solution. The corrosion morphology observations indicated that an increase in nanoparticle loading lead to an increase in the intercalation site and make the composite opaquer. Furthermore, the nanoparticles loading showed poor interaction with the epoxy composite, due to clustering of the nanoparticles and visible as wavy opaque surface. The findings show that the HNT is a very good alternative as a corrosion barrier in coating due to their viability and compatibility with diversity of water- and oil- based coatings onto a protected surface.

Keywords: Electrochemical impedance spectroscopy; Halloysite nanotube; Epoxy composite coating; Electrochemical Corrosion; seawater

1. INTRODUCTION

Aqueous corrosion represents the most troublesome problem encountered when in contact with sea water as a destructive attack to structures, ships and other equipment used in sea water services [1].

On the other hand, atmospheric corrosion is equally significant problem similar to the aqueous corrosion if the metal is exposed to the atmosphere nearby the coastlines, which require a systematic approach to counter them. Development of smart coating that can inhibit corrosion at primary stage and stop further damage due to corrosion in the long service is vital [2]. The smart coating must be able to sense the external environment and create an appropriate response by releasing the inhibitor [3]. Halloysite nanotube (HNT) has very low toxicity and a high biocompatibility; therefore, it is safe to be applied in various fields [4, 5]. HNT has numerous morphological forms, such as tubular, spheroidal, and platy. However, tubular form is the most prevailing morphology of halloysite [3, 6]. Zhu Shu et al. conducted the calcination of HNT before alkaline or acid treatment. The intention of the HNT calcination was to activate the silicate-aluminum network [7]. HNT calcination consists of an octahedral layer (AlO_6), a tetrahedral layer (SiO4), and a water interlayer. White et al. focused on a study to assess the effect of alkaline and acid treatment as a corrosion environment on HNT. The findings indicated that the acid treatment was effective in increasing lumen diameter [8]. The HNT clay mineral is getting popular in the self-healing materials due to the ability of their control and loading [9]. Chemically, HNT clay mineral is almost the same to Kaoline clay with multilayer tubular structure [10]. Various researchers studied the efficiency of HNT as healing agent and corrosion inhibitors to create a self-healing protective coating. HNT are recently the promising filler as the size of HNTs come with high variety among the clay nanoparticles. The compatibility of the inhibitor-loaded HNT with the host coating is an essential issue affecting the functions and stability of the developed smart coating [11]. However, the corrosion resistance of coatings in the presence of HNT has yet to be investigated.

Encapsulation and casting of electronic devices have widely utilized the usage of epoxy resin. Nanoparticle of silica filler was implanted into epoxy resin to enhance the thermal, mechanical and electrical properties of the material. Another option was to implant the silica into the epoxy-based matrix. It is the sol-gel process of a variety of alkoxysilanes by hydrolysis and condensation to process the silica particles and even the silica networks [12]. Material containing more epoxide group in the molecule of thermosetting matrix or resin materials is called epoxy. Epoxy is the representative unit of epoxy polymer as oxirane or ethoxyline, where oligomers of diglycidyl ether of bisphenol A (DGEBA) is nearly all the commercially available epoxy resin [13]. These oligomers will become thermosetting polymer and form a by-product with the hardener and then get cured. DGEBA is a commonly commercial epoxy resin.

A technique of applying a sinusoidal perturbation to a system is a frequency domain measurement called Electrochemical Impedance Spectroscopy (EIS). Electrochemical impedance spectroscopy is mainly the proficiency of a circuit element to resist the flow of electrical current as stated below the Ohm's Law. The evaluation of coating performance by extracting the characteristic parameters from Bode plots of the EIS has a useful theoretical and practical value.

This study aims to develop the active protection and barrier properties of HNT-epoxy composite coatings on X65 Carbon Steel. The effect of HNT on morphology, microstructure and corrosion behavior of epoxy composite coatings against 3.5 wt.% NaCl solution was investigated. HNT-Epoxy composite coatings were applied on the carbon steel substrate by brushing. Various amount of HNT was added to epoxy base coating, and then its electrochemical behavior was evaluated by using EIS to study corrosion protection mechanism. Furthermore, the corrosive morphology characteristic of the HNT-epoxy composite coatings was done by optical microscope and field emission scanning electron microscope.

2. MATERIALS AND METHODS

For EIS study, 15 samples (three samples for each test) were prepared with a dimension of 1cm × 1cm × 0.3cm to take an average amount for better accuracy. Pipeline raw material of X65 carbon steel was used as the metal substrate with a hollow cylindrical shaped and, a thickness and long diameter of 2.54cm and 60cm, respectively. The X65 carbon steel metal substrate was cut by using the hydraulic shearing machine and abrasive cutter into 1cm × 1cm × 0.3cm dimensions. The carbon steel samples were grinded with sandpaper and drilled to make a small hole for soldering purpose. Then, the carbon wire was soldered onto the sample and continuity function was used to test a solder joint. An exact amount of Halloysite nanotubes (HNT, purchased from Aldrich Chemistry) were measured and poured into a beaker. Acetone was poured into the beaker and continuously stirred using magnetic stirrer for at least 1 hour. Bisphenol A diglycidyl ether (BADGE) and M-xylenediamine (MXDA) with volume ratio of 2:1 were used as epoxy resin and hardener, respectively. A BADGE was mixed with the various content of prepared HNT and continuously stirred at 80^{o}C for 5 hours. Other than that, a certain amount of MXDA was mixed with the various content of prepared HNT and stirred for 15 minutes. In this research, the composite coating with and without HNT on the carbon steel substrate were applied by brushing. The coated carbon steel was cured for 1 week at ambient temperature and measured the thickness of coating on the carbon steel to get a uniform coating thickness of 120-200 µm.

The coated steel specimen, Ag/AgCl electrode and Ss316 Auxiliary were used as the working electrode (WE), reference electrode (RE) and counter electrode (CE), respectively. All tests were done in a 3.5 wt.% sodium chloride solution. Before the test, the WE was mounted in epoxy and plunged in the solution for 1 hour to obtain a steady state. Electrochemical detection methods based on EIS were performed in the range of frequency from 10000 to 0.01 Hz using a NOVA software. The amplitude of the sinusoidal voltage signal was 10 mV.

The morphology characterizations of the HNT samples were done by using the field emission scanning electron microscopy (FESEM; FEI/Nova NanoSEM 450) at ambient temperature.

3. RESULTS AND DISCUSSION

In order to carry out the electrochemical impedance spectroscopy study, Nyquist diagrams and Bode plots measured on an X65 carbon steel electrode coated with the epoxy composite coating with various content of HNT were used. As shown in Figure 1, the low-frequency impedance in the higher concentrations of prepared HNT is larger compared to that evaluated on the lower concentrations at individual time until a certain limit. The low-frequency impedance value shows a high value at 5 wt.% and 10 wt.%, compared to other contents. The significant difference between the impedance values indicated the effectiveness of the composite coating toward corrosion protection. Thus, corrosion resistance was enhanced by the addition HNT to the epoxy coating. The low-frequency time-constant can be related to the charge transfer at the interface of steel and epoxy coating, and the high-frequency one can be attributed to the capacitive behavior of the coating. The coating can make adequate protection over the substrate carbon steel from corrosion. With increasing immersion time up to 72-hours, the coatings were degraded, and corrosive species reached the carbon steel-coating interface, resulting in the reduction of the low-frequency impedance.

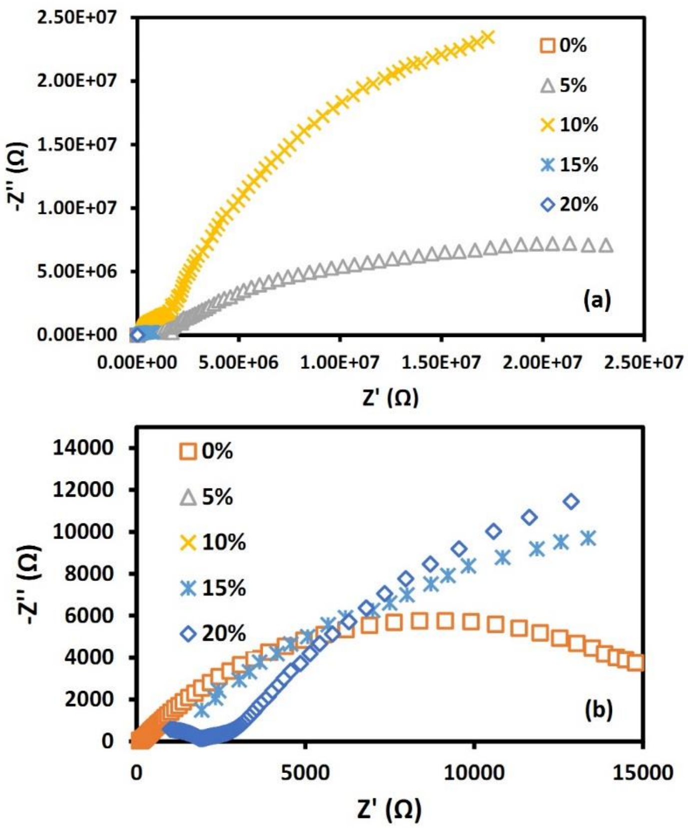

Figure 1. Nyquist plots of various amount of HNT in epoxy composite coating against corrosion in 3.5% NaCl solution.

Furthermore, the high-frequency capacitive behavior reduced and gradually superseded by the resistive behavior. The impedance semicircle at medium-frequency part can be associated to the corrosion effect on the electrode surface, indicating the corrosion layer resistance. Then, the deposit layer can affect more corrosion which lead to a change in the corrosion of steel under mechanistic coating with time in the system. Commonly, the resistance enhancement of corrosion in epoxy coating by addition of nano-fillers can be attributed to the better adherence and improve barrier performance of the coating. In the HNT epoxy coating, the halloysite behaved as a good barrier by decreasing the porosity of the epoxy coating resistance. When the halloysite concentration increases, the barrier effect enhances and increases the ability to protect corrosion coating.

Theoretically, the intersection points between line of Bode phase and Bode modulus will move toward the upper left area from lower right area, as the coating performance increase [14]. As shown in Figure 2, the intersection points move toward the upper left area from the concentrations of 0 wt.% to 10 wt.%, which is collateral with the increment of coating performance. Then, the intersection points move toward the lower right area from the concentrations of 10 wt.% to 20 wt.% which can be related to the decrement of coating performance. As a result, there was a decreasing tendency on the phase angle and the coating resistance at the middle frequency range of 1 to 1000 Hz. Therefore, the phase angle displayed a significant reduction with increasing concentration. The phase angle is one of the transparent element in determining the coating performance which can be easily extracted from the high frequencies. Therefore, interpretation results between the coating resistance and phase angle can be used to identify the coating degradation [15]. Nevertheless, since an electrical model should be fitted from the EIS measurement, there is a possibility of error in extraction of coating resistance and the coating capacitance. But, when the phase angle extract directly from the Bode plots at high frequencies, there should not be an error [16]. To determine electrochemical corrosion parameters and quantitative properties of the coating, the measured impedance data was fitted by electrochemical equivalent circuits.

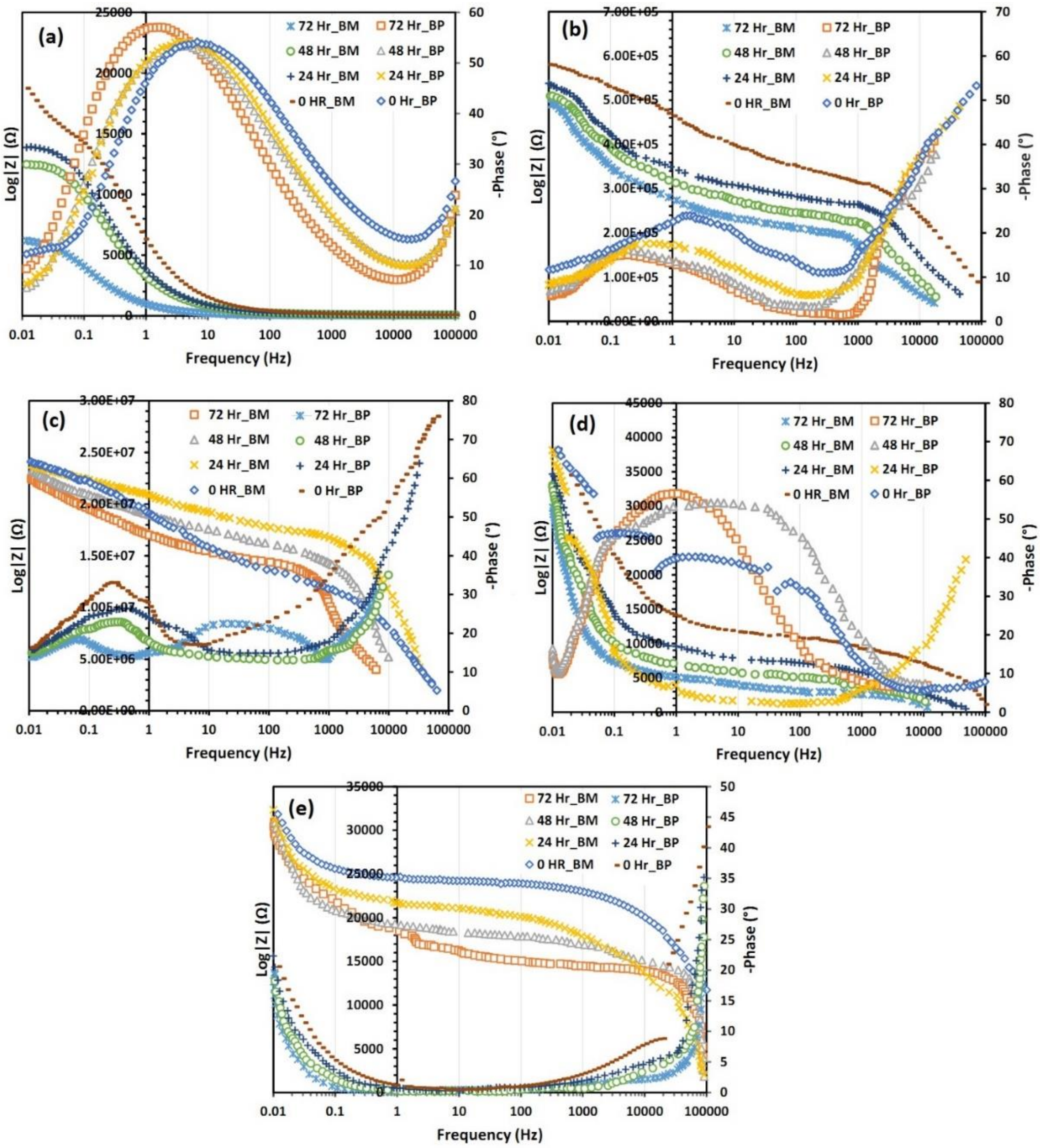

Figure 2. Bode plots (a) 0 wt.%, (b) 5 wt.%, (c) 10 wt.%, (d) 15 wt.%, and (e) 20 wt.%, of HNT in epoxy composite coating against corrosion in 3.5% NaCl solution.

Table 1. EIS results of HNT-epoxy composite coating against corrosion in 3.5% NaCl solution.

Parameters	0 wt.%	5 wt.%	10 wt.%	15 wt.%	20 wt.%
R_{sol}	42.416	-1796.7	-6270.6	-32034	-1226.8
R_{pore}	12839	5.17E+05	1.16E+06	35655	3470.4
C_{coat}	8.26E-05	1.22E-10	1.06E-10	7.28E-08	8.73E-07
N	0.68997	0.9148	0.92859	0.25955	0.39309
R_{PL}	1.10E+12	1.02E+07	4.58E+07	1.59E+05	1.10E+12
C_{DL}	0.089852	5.14E-07	3.37E-07	0.00020441	0.00033947
N	1.1	0.70643	0.44765	0.75754	0.57034
χ^2	1.2483	0.3932	0.57952	0.040779	0.28403
EEC	[R(Q[R(RQ)])]				

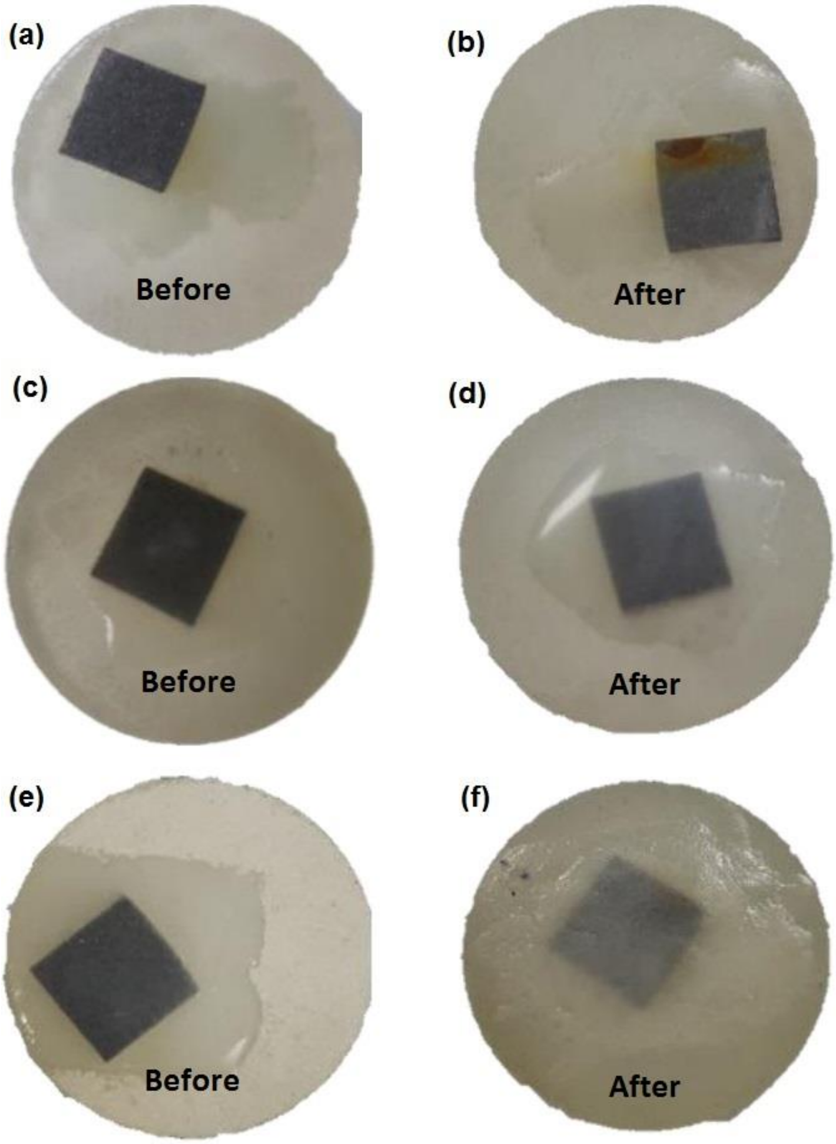

Figure 3. Optical images of (a), (b) 0 wt.%, (c), (d)10 wt.% and (e), (f) 20 wt.% HNT-epoxy composite coating before and after EIS test against corrosion in 3.5% NaCl solution.

A constant (non-intuitive) phase element (CPE) is utilised to replace capacitance to study the heterogeneous surfaces of the coated electrodes [11]. R_{sol}, R_{PL} and R_{pore} are solution, charge-transfer, and coating resistances, respectively. C_{DL} and C_{coat} are CPE of double-charge layer and the coating, respectively. After the test, the impedance data was fitted by the circuit to consider the interfacial behaviour. Table 1 shows the EIS results of HNT-epoxy composite coating against corrosion in 3.5% NaCl solution. The C_{coat} value increases gradually with time which indicates an increase in water absorption. The R_{PL} and C_{DL} values indicate that water had reached the substrate. The R_{PL} value reduces and the amount of C_{DL} increases slightly; these changes represent a small increase in corrosion and filling of the pore in the metal substrate. The R_{pore} value is significantly decreased as water penetration through the pores, indicating a slow demolition with increasing exposure. The decrease in the C_{coat} values indicate that the composite coating steel is rejecting water from the coating [17].

The morphology of the coated steel electrodes with various concentrations of the prepared HNT in 3.5wt-% NaCl solution are shown in Figure 3. As the HNT content increases in the coating, the deterioration area on the carbon steel surface decreases.

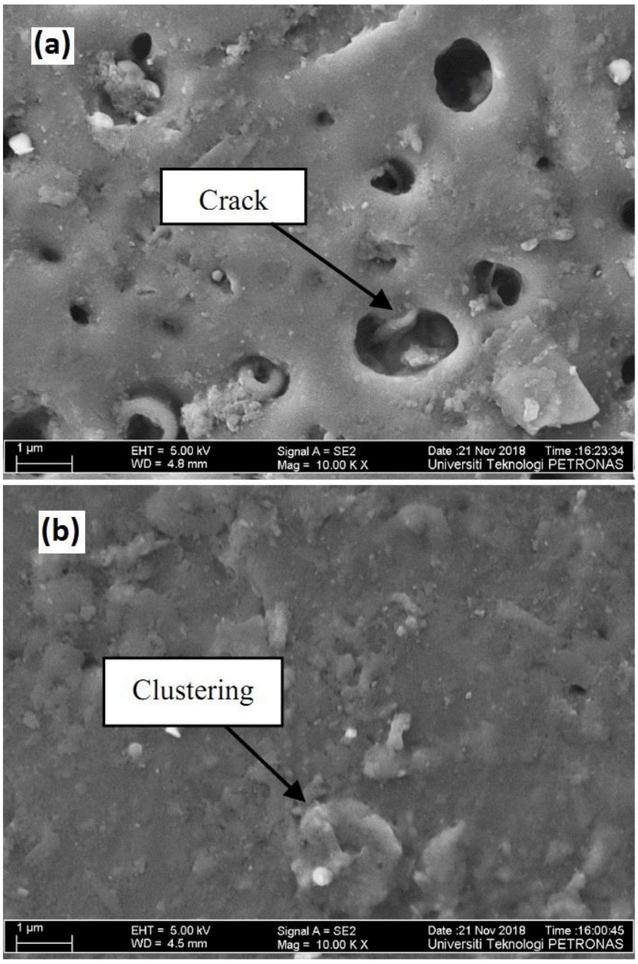

Figure 4. FESEM images for 0 wt.% and 10 wt.% of HNT-epoxy composite coating against corrosion in 3.5% NaCl solution.

This finding is consistent with the results of impedance that the addition of Halloysite can improve the corrosion protection ability of the composite coating. Besides, the morphological observation indicated that chemical reaction occurs and the corrosive solution permeates under coating. The epoxy coating with 20 wt.% HNT reveals the best corrosion resistance and the minimal area of corrosions among the various HNT contents in the coatings. The accumulation of nanoparticle within the composite coating has resulted in the opacity of the composite coating and intercalated– flocculated arrangements [11, 18]. The FESEM images in in figure 4 indicate that the surface of the 10 wt.% composite coating have many craters, which shows the existence of HNT on the coating surface. The surface of exposed control epoxy coating shows severe void formation and the degradation on the surface of without HNT epoxy coating is not uniform.

Therefore, formed defect leads to the water penetration through the composite coating into the carbon steel substrate. Incorporation of HNT to the epoxy monomer aids to better protection of the bulk coating for longer period of time. The HNT protects the epoxy polymer from formation defects. Consequently, the HNT ability to provide a long-term stability for the coating was proven [19].

These findings show the high surface roughness value of 10 wt.% HNT epoxy coating compared to the controlled sample.

4. CONCLUSION

EIS is a powerful method to study the corrosion protection of stainless steel. In this research, the effect of HNT-Epoxy composite coating on carbon steel against corrosion in 3.5% NaCl solution was investigated. The EIS analysis of the corrosion protection of HNT-Epoxy composite coating on X65 carbon steel indicated that the low-frequency impedance of composite coatings increased with the increase of the HNT concentration into the epoxy composite coating until a certain limit in the Nyquist plot. As shown in Bode plots, the intersection points between line of Bode phase and Bode modulus moving toward the upper left area which is collateral with the coating performance until a certain limit. Both the Nyquist plot and Bode plot show a turning point of the composite coating from good to poor corrosion resistance performance. The corrosion morphology observations indicated that an increase in nanoparticle loading leads to an increase in the intercalation site and makes the composite opaquer. Furthermore, the nanoparticles loading show poor interaction with the epoxy composite, due to clustering of the nanoparticles and visible as wavy opaque surface.

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