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INVESTIGATION ON PERFORMANCE OF EPOXY COATED STEELS WITH NANO-SIO_2 AND POLYANILINE COMPOSITE USING COMPLEX IMPEDANCE SPECTROSCOPY

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ABSTRACT: This study was conducted to characterize an anti-corrosive epoxy coating for steel with Nano-SiO_2-Polyaniline (PANI) composites using low impedance spectroscopy. The epoxy coating was modified using a varying concentration of nano-filler combination. Coated steels were dipped in 3.5 wt% NaCl solution to induce corrosion. Impedances were measured from 20 Hz to 20 MHz. The electrical characterization was related to the coating performance of epoxy coating with varying concentration. The Nyquist and Bode plots were displayed and related to the graphs with the coating resistance and capacitance. Based on Nyquist plots, 40-60% combination of Nano-SiO_2 and PANI has the largest semi-circle curve, while on Bode plots, still, the 40-60% combination has the largest magnitude of impedance and phase angles. Equivalent circuit model was fitted to measure directly the coating resistance and coating capacitance of the coated steel. Based on the equivalent circuit model, the 40-60% of Nano-SiO_2 to PANI combination had the highest coating resistance equal to 9.50E7 ohms, and lowest coating capacitance of 2.0E-12 Farads. The results presented that all combinations have better corrosion protection performance compared to that of pure epoxy coated steel.

Keywords: Nanosilica, Polyaniline, Impedance, Epoxy Coating, Corrosion

1. INTRODUCTION

Chloride-induced corrosion of steel bars is one major concern of the construction industry where the chemical attack reduces the life span of the structure. At the start of the 1970's, several researches have started to resolve the corrosion problem of structural materials (steels bars, reinforced concrete, etc.) at the high-chloride environment. Different techniques have been used to reduce corrosion. Epoxy coatings are applied to steel bars to provide a protective layer against chloride penetration. Epoxy coatings generally reduce the corrosion of steel bars subject to an acidic environment in two ways: (1) the epoxy coatings act as a physical protective barrier layer to minimize the ingress of oxygen, water and ions, and (2) the epoxy coatings serve as a reservoir for corrosion inhibitors to resist the chloride attack [1].

In the advent of nanotechnology and incorporation of nanomaterials into existing products, researches involving nanomaterial-based anti-corrosion coatings have steadily gained interest generating more than 2500 publications as of 2018 [2]. Nanotechnology developed advanced hybrid composites to enhance properties of such composites and had a significant role in managing steel corrosion [1]. Various technologies used nano-sized additives for anti-corrosive coatings and effectively reduced the corrosion risk of steels. The use of nanoparticles in producing coatings was reported to be cost-effective and easy-to-implement as they provide long-term corrosion protection.

Meanwhile, one trend in nanotechnology is the use and synthesis of nano-silica from organic waste products. Organic induced coatings are generally used to protect steel structures against corrosion due to their barrier properties which prolong diffusion of corrosive species into the coating and metal interface but they are still permeable to potentially corrosive species such as oxygen, water and aggressive ions [3]. Because of its stable structure, nano-silica is a widely used material in the construction industry where it acts as filler or binder. At present, nano-SiO_2 is fabricated from silicon-containing biomass materials for thermal energy efficiency and synthetically produced in the form of ultra-fine particles of amorphous silica averaging 20 nm in diameter.

Many studies showed that silicate coatings provide good corrosion resistance for the structural metals and are safe for human and environment [4]. Compact silicate layers increase corrosion resistance with increasing curing time. The surface modification by silica can lead to a better dispersion of particles and fewer agglomerates In return, it results in better corrosion resistance. Polymer-based coatings have been reported as good candidates as polymers are chromate-free and can have outstanding processability, excellent chemical resistance and strong adhesion to the various metallic substrate [5].

Polyanilines (PANI) are conducting polymers and have been an interesting study for its wide range applications and one of which is on corrosion resistance [6]. PANI is well known in many applications such as chemical sensors, battery electrodes, supercapacitors and antistatic coatings.

Due to the unique physical protection, high resistance, low cost and no negative impact on the environment, PANI can be used in aviation, marine and special conditions. PANI is a new type of metal corrosion protection material with high commercial prospects, however, it has a high rigid molecular chain and has strong interactions between chains. Thus, it has poor mechanical properties that restrict its development [7].

The modification of the epoxy resin using the combination of nano-silica particles from organic materials and polyaniline as nano-fillers, epoxy coating were prepared usually by dispersion of nano-composites into the epoxy matrix. These nanoparticles were expected to enhance the surface morphology and anti-corrosion behavior of the epoxy coating.

Nowadays, researches are using non-destructive techniques to evaluate the corrosion activity of steel bars. One of which is the complex impedance spectroscopy (CIS). For years, studies on degradation and failure mechanisms can be predicted using its electrochemical behavior. This technique uses electrical properties to characterize the coating resistance from chloride ions using a wide range of frequencies.

Impedance measurement can be processed into resistive and capacitive elements depending on the electrical behavior of the sample. The results of impedance measurement are shown via changes of the dielectric properties of the coating [8]. Many researchers have applied CIS to analyze concrete durability in terms of corrosion resistance and corrosion capacitance.

The impedance modulus at low frequency (|Z|) is an appropriate parameter for characterizing the protective properties of the coatings [9]. The impedance data will demonstrate the changes in capacitance and resistances. The higher the value of coating capacitance, the more current is conducted passing through the capacitor. This response shows a capacitive behavior.

The general objective of the study is to create and characterize an anti-corrosive epoxy coating to steel with nano silica-polyaniline composites using low impedance spectroscopy. Specifically, it aims to combine nano-silica and polyaniline (PANI) and create an anti-corrosive coating due to chloride ingress that can be applied to steel metals. Also, this study is expected to investigate and characterize the effectiveness of the coating in steel using low impedance spectroscopy by determining the coating capacitance and coating resistance. In this study, the combination of nano-silica particles from rice hull ash and polyaniline (PANI) as nano-fillers to form polymer composites serves as a potential anti-corrosive epoxy coating to steel. This research is interested in increasing the properties of polymer composites by combining two different kinds of particles such as nano-silica from rice hull ash and a conducting polymer, PANI.

2. MATERIALS AND METHODS

The study was designed to determine the performance of coatings with different combinations of nano-SiO_2 and PANI.

2.1 Materials used

2.1.1 Steel

Round steel bars with 16-mm diameter were obtained and cut into smaller pieces having a thickness approximately equal to 5 mm.

2.1.2 Nano-SiO_2

The nano-SiO_2 powder was synthesized and obtained from Nano-science and Technology Facility Instrumentation and Analytical Services Laboratory at the Institute of Chemistry, University of the Philippines Los Baños**.**

2.1.3 PANI

The PANI powder has obtained the Institute of Mathematical Sciences and Physics of the same university.

2.2 Preparation of Coating

The two (2) powders were mixed using a solution blending method where a solvent was used to disperse the silica-polymer composition [10]. The concentration of the composites material was 5% by weight of the epoxy coating and varying concentration of nanoSiO_2-PANI materials: 80%-20%, 60%-40%, 50%-50% and vice versa. Epoxy coating (VT-512 Multi-Purpose Epoxy) comprised of 1:1:1 ratio (50% reduction) of epoxy resin, epoxy hardener and epoxy reducer were mixed simultaneously together with nano-composite materials. Each concentration has 20 grams epoxy coating including the nano-composite materials.

2.3 Preparation of Coated Steel Specimen

The steel bars were washed using acetone to remove existing grits, rust and oil. Afterward, the steel was coated by the epoxy coating using dip-coating method at controlled speed and time. The coated steel bars were immersed in 3.5 wt% NaCl solution using wet-dry cycles (30 minutes exposure with 10 minutes drying) for 3 cycles. Three (3) trials were performed. Table 1 shows the percentage of the nano-composite materials in 20 grams epoxy coating while Fig. 1 shows the coated specimens.

Table 1 Mix proportion of coatings

LABEL	NANO-SiO2 (%)	PANI (%)
PURE EPOXY	0	0
A	80	20
B	60	40
C	50	50
D	40	60
E	20	80

Fig. 1 Coated specimens subject to drying

2.4 Measurement of Impedance

Coated steels were placed in the impedance analyzer. The real and imaginary impedances were obtained using the non-contacting method of the Keysight Impedance Analyzer E4990A. The frequency region ranges from 20 Hz to 20 MHz. Impedance, coating resistances and coating capacitance were modeled and assessed using the electrochemical impedance spectroscopy diagrams and equivalent electrical circuit model that shows the evolution of impedance spectra over time. steel bars with 16-mm diameter were obtained and cut into smaller pieces having a thickness approximately equal to 5 mm.

3. RESULTS AND DISCUSSION

3.1 Coating evaluation

Complex Impedance Spectroscopy (CIS) was used to investigate the corrosion performance of steels coated with varying concentration of nano-composites. The results were analyzed in terms of Nyquist plot and Bode plot.

Nyquist plots are commonly used because these plot formats illustrate ohmic resistance effects. The shape of the curve is often a semi-circle and it is easier to extrapolate the plot in order to read the respective ohmic resistance. However, the Nyquist plots do not use frequency data. The measured real and imaginary components of impedances, Z' and Z" respectively, of the five (5) combinations and pure epoxy coated steels were plotted and shown in Fig 2. It is evident that the Nyquist plots of the impedance response of the coated steels showed the marked difference with varying concentration of nano-composites. The effect of nano-silica and PANI concentration changed the position and size of the semi-circular plot. The larger the diameter of the semicircle indicates higher corrosion resistance of the epoxy coating.

Based on the Nyquist plot, all five combinations (A to E) exhibited larger semicircles compared to PURE epoxy coating. Among the five combinations, combination D (40% Nano-SiO_2 and 60% PANI) generated the largest semicircle diameter while combination C (50% Nano-SiO_2 and 50% PANI) generated the smallest diameter.

The other representation shown in the results of this study is called Bode diagram which shows the logarithm of the impedance modulus (log|Z|) and the phase angle displacement (ϕ) as a function of the logarithm of the frequency. The impedance modulus at low frequency (|Z|) is an appropriate parameter for characterizing the protective properties of the coatings [7].

The impedance modulus and phase angle displacement at different frequencies are shown in Fig. 3 and Fig. 4 respectively. Based on these figures, all five combinations showed relatively higher impedance at the low-frequency region while showing relatively higher phase angle at the high-frequency region. Again the 40-60% combination of nano-silica and PANI (D) showed the highest impedance and phase angle response and therefore showed the highest protective character compared to the other combinations. Polyaniline has been widely used as components of nanocomposite coating formulation due to catalytic activity to form a passivating oxide layer [11]. On the other hand, the addition of nanosilica in the nanocomposite coating increases the superiority of polyaniline as a passivating layer in anticorrosion formulations [12].

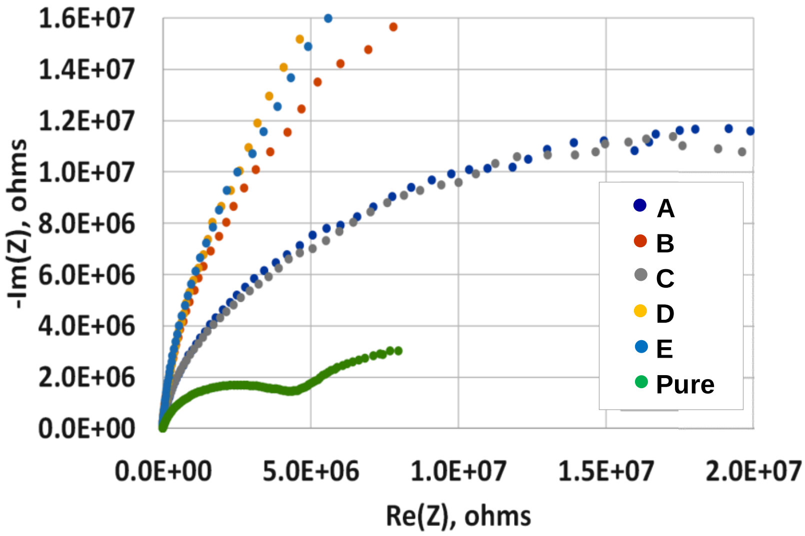

Fig.2 Nyquist plots for the different combinations

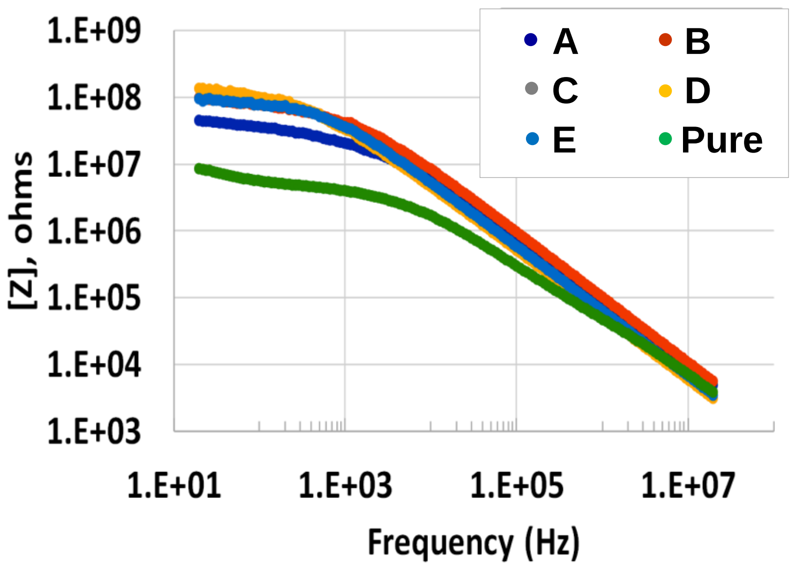

Fig. 3 Log |Z| vs Log Frequency of different combinations

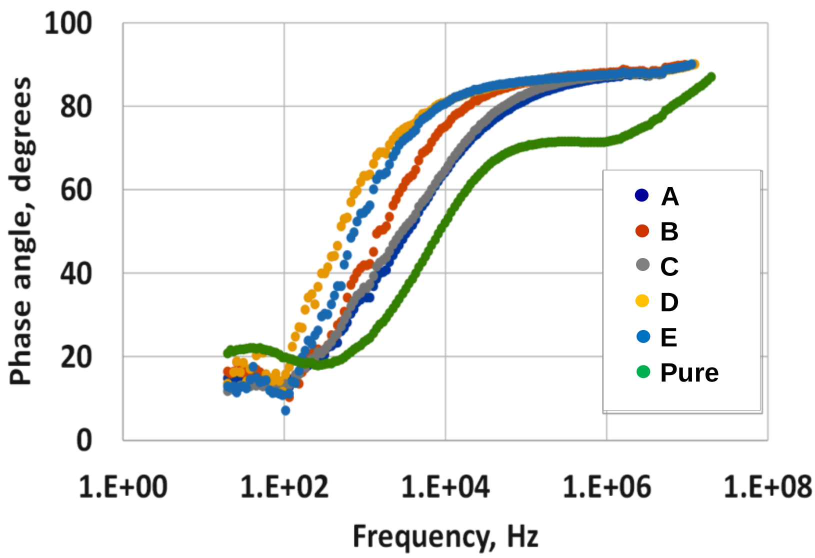

Fig. 4 Phase Angle vs Log Frequency of different combinations

3.2 Equivalent circuit model

Another tool for interpreting EIS data is through an equivalent circuit model or ECM. It involves the fitting of the EIS response of a system of the passive network. It is possible to create the ECM because the transfer function of the impedance of a network can be arranged to match the impedance response of the study. EIS equivalent circuit model-fitting has been used as a powerful technique that allows electrical fingerprinting providing an insight into properties and behavior of a large verity of materials [13].

The EC-Lab Demo was used as the fitting software and Igor Pro 6.12 as the plotting software. The equivalent circuit model used is shown in Fig. 5. It was based on the available parameter circuit in the software

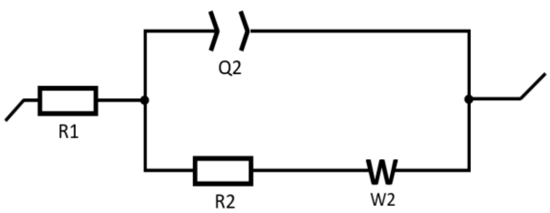

Fig. 5 Equivalent circuit model of epoxy-coated metal

Using the Nyquist plot, the equivalent circuit model was fitted and the circuit parameters were determined using plotting software. According to research, the value of coating resistance, R_P,or R_2 is the best measurement of coating degradation, which can be found from semthe i-circle diameter of the Nyquist plot. R_p represents the charge transfer resistance. The values of CPE or Q_2 and R_2 were measured and provided by the instrument and summarized Table 2.

Table 2 Fitting results of EIS plots for coated steels

LABEL	Cc (Farads)	Rp (ohms)
PURE EPOXY	2.50E-10	4.00E+06
A	2.80E-11	3.30E+07
B	3.50E-12	6.60E+07
C	3.50E-11	3.05E+07
D	2.00E-12	9.50E+07
E	3.50E-12	7.10E+07

From Table 2, combination D has the lowest coating capacitance, 2.00E-12 Farad and highest coating resistance equal to 9.50E+07 ohms. Combinations B and E have the same coating capacitance, while combination E has the second-highest coating capacitance. PURE EPOXY showed lower performance compared to any of the combinations.

4. SUMMARY AND CONCLUSIONS

This study was conducted to create an anti-corrosion epoxy coating with nano-composite materials and investigate its performance using low-impedance spectroscopy. Nyquist and Bode's diagrams were used to evaluate the visual presentation of impedance. Equivalent circuit model was established to match the measured data and control the impedance model. The electrical components/parameters led to establishing the relationship between the model and measured spectra.

Based on Nyquist diagrams, combination D (40% Nano-SiO_2 – 60% PANI) has the largest diameter and is, therefore, the most effective coating combination. Combinations C (50%-50% Nano-SiO_2-PANI) and A (80%-20% Nano-SiO_2-PANI) have the smallest diameter and least coating resistance, next to the pure epoxy coated steels.

Results of the Bode plots show that the combination D (40%-60%) and E (20%-80%, Nano-SiO2-PANI) have the largest coating resistance and least coating capacitance. The charge conductivity significantly decreases with a higher concentration of PANI.

From the equivalent circuit modeling, the capacitances and resistances were found to have a respective direct and inverse dependence with nano-SiO_2 and PANI concentration. Combination D had 2.00E-12 F as its coating capacitance and 9.50E+07 as its coating resistance. Combination D thus showed superior protection performance compared to the other combinations.

Overall, all combinations of varying concentrations of Nano-SiO_2 and PANI effectively protected the steel against corrosion. Generally, the nano-composite coatings were proven to offer corrosion protection for the steel. It acts as a barrier to ions which resist the corrosion attack. As a result, the destructive effects of chloride ingress through structures can be mitigated.

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