CAAP Quarterly Report

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Prepared for: *U.S. DOT Pipeline and Hazardous Materials Safety Administration*

Project Title: Development of New Multifunctional Composite Coatings for Preventing and Mitigating Internal Pipeline Corrosion

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For quarterly period ending: *Dec. 31th, 2018*

Business and Activity Section

(a) Generated Commitments

No changes to the existing agreement

(b) Status Update of Past Quarter Activities

The research activities in the 9th quarter continuing efforts by characterizing the nano-modified coatings and assess their long-term performance, as summarized below.

Tasks 5-7: Summary of Characterization of the new coating systems and performance assessment

7.1 Objectives in the 9th Quarter

The overall results from the previous work suggested that the addition of nanofiller into plyometric matrix could led dramatic improvements on tribological, mechanical, and electrochemical properties. The salt fog test was employed to study the long-term corrosion protection performance of the new coating systems. In this report, the EIS data was analyzed by electrical equivalent circuit technique, as this technique is capable of providing a better understanding of the delamination process of the coating during corrosion attack.

7.2 Experimental Program in the 7th Quarter

7.2.1 Experimental design

The experimental study was salt fog test for nanofiller coatings, and accordingly the electrical equivalent circuit analysis on EIS results.

7.2.2 Characterization using Electrical equivalent circuit (EEC) technique

Based on literature studies, the Electrical equivalent circuit (EEC) model was widely used to interpret the EIS results [1]–[7]. The model can be fitted based on the impedance and phase angle curves in the Bode plot. The corrosion phase can be classified into four stages, and each of them is represented by one EEC model, as illustrated in Figure 1.

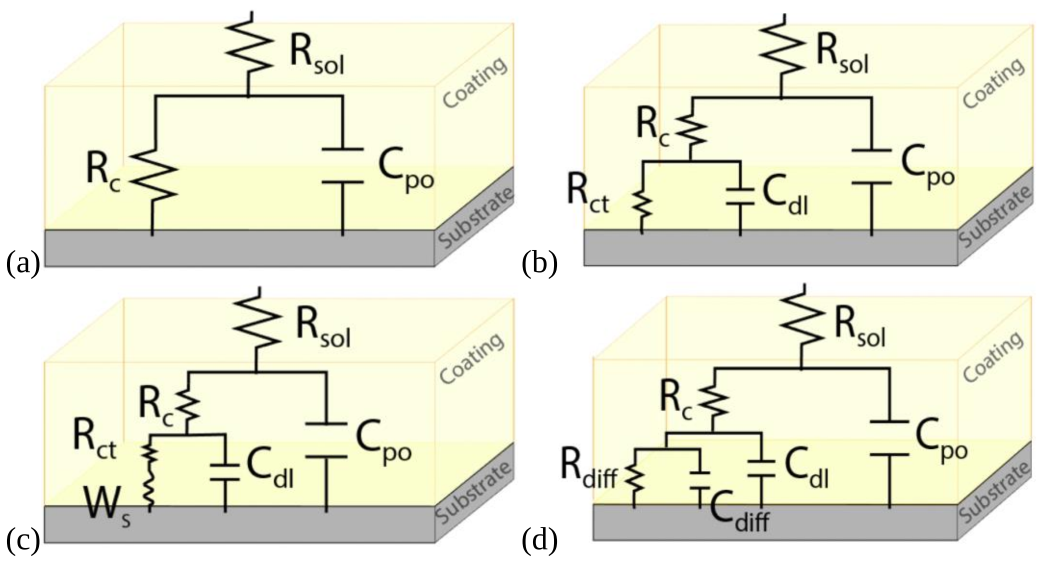


Figure 1. Electrical equivalent circuit models for (a) stage I, model A, (b) stage II, model B, (c) stage III, model B with Warburg element, (d) stage IV, model C

Four stages, illustrated in Fig. 1, could be summarized as below:

- Stage I: Model A was used to present the initial stage, which the coatings were intact film and behave as an isolated protective layer for corrosion protection. At this stage, the equivalent circuit model includes R_{sol} solution resistance, R_c coating resistance and C_{po} constant-phase element of the coating, indicating the corrosive medium could not penetrate the coating layer.
- Stage II: Model B was employed to represent the initial stage of corrosion reaction, while the electrodes were able to penetrate the coating layer to contact with the metal substrate, and

corrosion reaction has been begun. Compared with model A, R_{ct} charge transfer resistance and C_{dl} constant phase element of the double-charge layer were added in the model to simulate the coating-substrate interface.

- Stage III: At stage III, Model B with Warburg impedance element (W) is included in the electrochemical equivalent circuit when the diffusion effect dominates corrosion. The Warburg element indicates that the electrochemical corrosion reaction in the coating-substrate interface is diffusion-controlled.
- Stage IV: The model C can be used to confirm the results, which new parameters of constant phase element of diffusion capacitance (C_{diff}) and diffusion resistance (R_{diff}) were included. At this stage, severe corrosion damage has occurred and which a thin corrosion product layer was accumulated in the coating-substrate system.

7.3 Results and discussion

7.3.1 Characterization of Neat epoxy under salt fog test

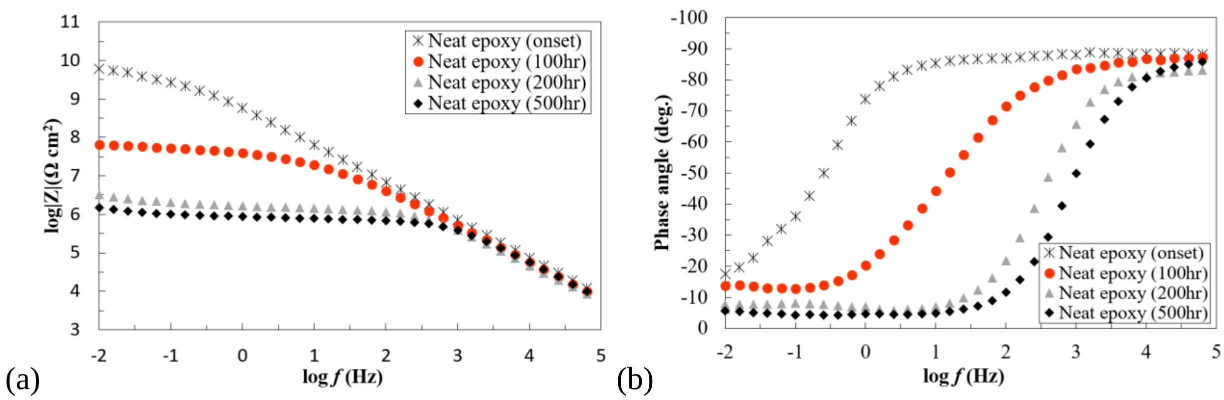


Figure 2. Impedance curve (a) and phase angle curve (b) of the neat epoxy group

The results of the neat epoxy group were employed as a reference for all the nanofiller coatings, as typical degradation process was observed in the samples during the Salt fog test. A typical degradation process of a coating film should be observed from both impedance and phase angle curve in the Bode. As the exposure time elapsed, the following changes could be observed in a typical degradation process of a protective coating film.

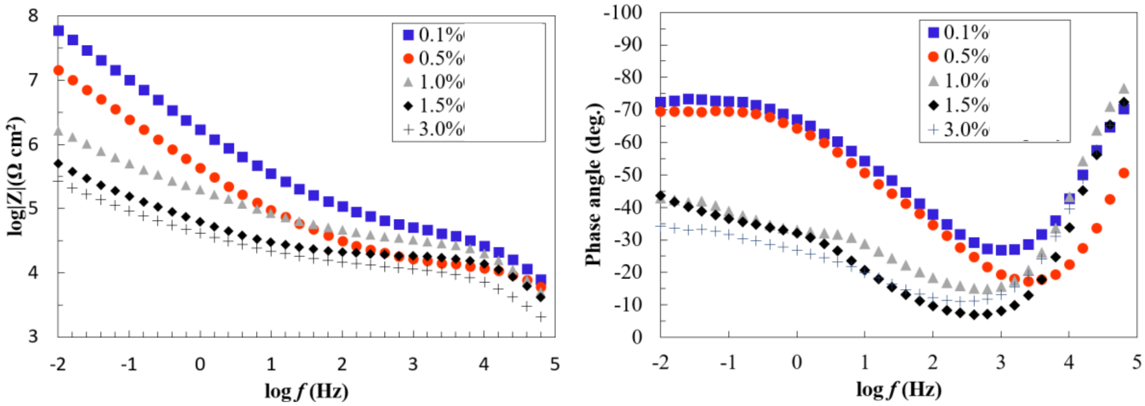
The observations of the neat epoxy group during the exposure could well fit the suggestion above:

a) In the impedance curve, the Zmod value was continuously decreased with the increase of exposure hours. As illustrated in Figure 2, the impedance value has dropped.
b) The frequency value for the minimum phase angle has shifted 0.01 Hz to 100 Hz.

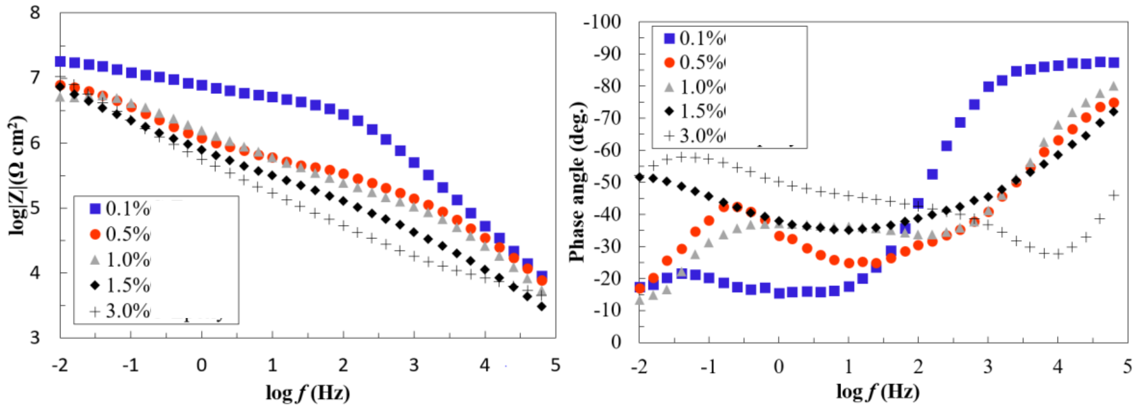
Subsequently, the electrical equivalent circuit (EEC) model could be determined by interpreting the impedance and phase curves. The EEC model could also be used to demonstrate the degradation process of the neat epoxy coating, which was illustrated in Figure 1. At the fresh stage, model B with Warburg impedance element (W) was introduced to fit the EIS data. It appeared that there were diffusion paths for the electrolyte to reach the coating-substrate interface and initiated coating degradation. After 500 hours exposure, model C was suitable for the neat epoxy sample due to the accumulated corrosion products at the coating-substrate interface.

7.3.2 Characterization of nanocomposites under salt fog test

Figure 3 has shown the Bode plots for the nanocomposite coatings. Compared with neat epoxy, a reduction of impedance value was observed at lower frequency region of impedance plots, and it is observed that the values were gradually decreased with higher content in the composites. The electrical resistance of the coatings was reduced by the high conductive network of nanoparticles.



(a) Impedance curve and phase angle curve at initial stage

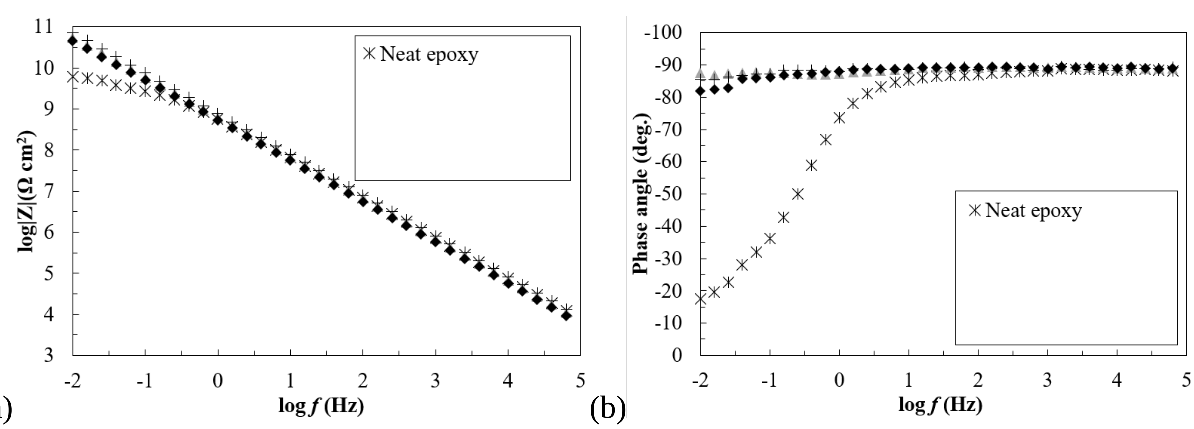


(b) Impedance curve and phase angle curve at 100 hours

Figure 3. Impedance curve and phase angle curve of the nanocomposite coatings (a)-(b).

7.3.3 Modified epoxy resin

(a) Corrosion barrier performance: EIS



(a) (b)

Figure 4. Impedance curve (a) and phase angle curve (b) of the new coatings at the fresh stage

All prepared modified epoxy coating demonstrated high impedance value at the low-frequency region, and phase angle was around 90 degrees in both high and low-frequency region. The impedance and phase curves for the tested groups were excellent.

(b) Contact angle test

The results from the contact angle test confirmed that the new coating would significantly increase the water repellency of the epoxy composites. The contact angle has increased from 26 degrees to around 110 degrees.

(c) Description of any Problems/Challenges

No problems are experienced during this report period

(d) Planned Activities for the Next Quarter

The planned activities for next quarter are listed below:

- As proposed, long-term performance experiment would be planned. Figure 5 illustrated a designed accelerated flow instrument, which contained a liquid reservoir, pump, and a long pipe. The performance of the tested samples will be evaluated, and detailed experimental results will be provided after the test.

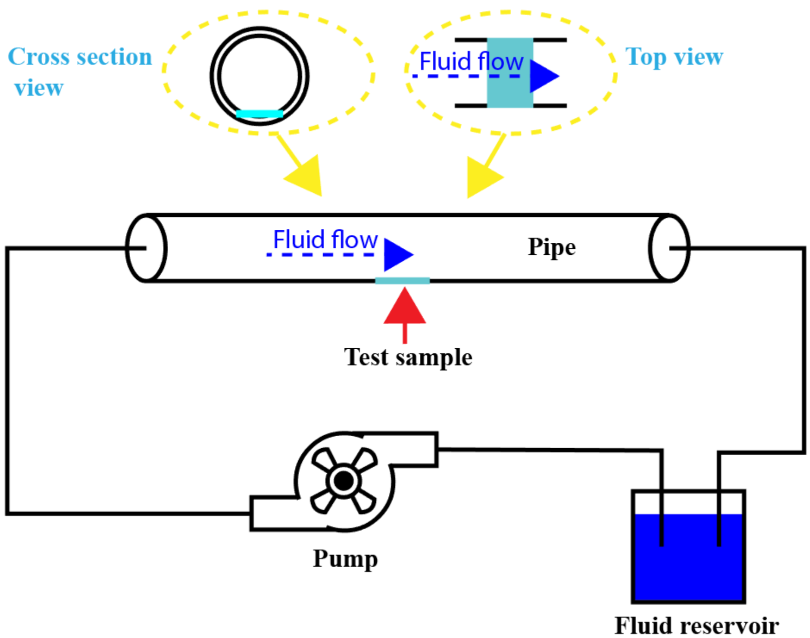


Figure 5. Schematic of the designed accelerated flow instrument