CAAP Quarterly Report

Date of Report: *June. 30th, 2017*

Contract Number: *DTPH56-16-H-CAAP03*

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

Prepared by: *North Dakota State University*

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For quarterly period ending: *June. 30, 2017*

Business and Activity Section

(a) Generated Commitments

No changes to the existing agreement

Purchase made for nano-materials and Q-panels over this reporting period

Purchase made for a latest high-speed mixer over this reporting period (cost from other grant-Dr. Lin's start-up)

(b) Status Update of Past Quarter Activities

The research activities in the 3rd quarter include refined work of material screening after learnt from the second report, nano-modified additives synthesis and characterization in Task 2, as summarized below.

<u>**Task 2: Synthesize, characterize and optimize the new coatings**</u>

In the previous reports, the recent studies have confirmed that use of nanomaterials in polymer prime could enhance different properties of a coating. Particularly, the literature supports that the addition of nanoparticles could have improvements in corrosion resistance, as well as mechanical properties. This stage aims to specify the nano-modified additives on the basis of the properties of the corrosion resistance at both short-term and long-term performance, from formulation to characterization. Identified test methodology in the previous reports is used in this stage for characterizing the new coating. Dissemination of the research has been achieved through internationally invited talks and high school student outreach. **Summary of work for Tasks 2.2 and 2.3 in the nano-modified additives and characterization.**

2.1 Formulation of nano-modified coating

As identified in the previous report, the nanoparticles could be great candidates to develop new high-performance coatings. In this stage, we aim to formulate and characterize nano-modified coatings. Note that conventional epoxy is used as the prime. It is mainly because to select the epoxy instead of other high-performance polymer prime is to gain better understanding of nano materials and their performance in a coating. The another line of the study is overlapped to explore the high-performance polymer primes reinforced with the nano-materials on the basis of these findings and will be docemented in the following reports.

2.1.1 Sample preparations and dispersion

Two dispersion methods have been carried out to find out how to enhance the dispersion and alignment of nanoplatelets in an epoxy matrix. Ultrasonication was used in both methods and solvent was also evaporated before mixing with a curing agent. Fig.1 (a) is showing a sample without ultrasonication. For the samples without evaporation of the solvent before mixing with a curing agent, an example is shown in Fig.1 (b).

Figure 1 Sample without ultrasonication (a)   without evaporation of solvent (b)

In the first method, the nanoplatelets were dispersed into a mixture that containing EPON 828 and 20 wt.% of xylenes. Ultrasonication was applied in the dispersion process at 100% amplitude with a duration of 60 mins. Misonic S1805 sonicator with a 3/4" probe was used in this process like shown in Figure *2*.

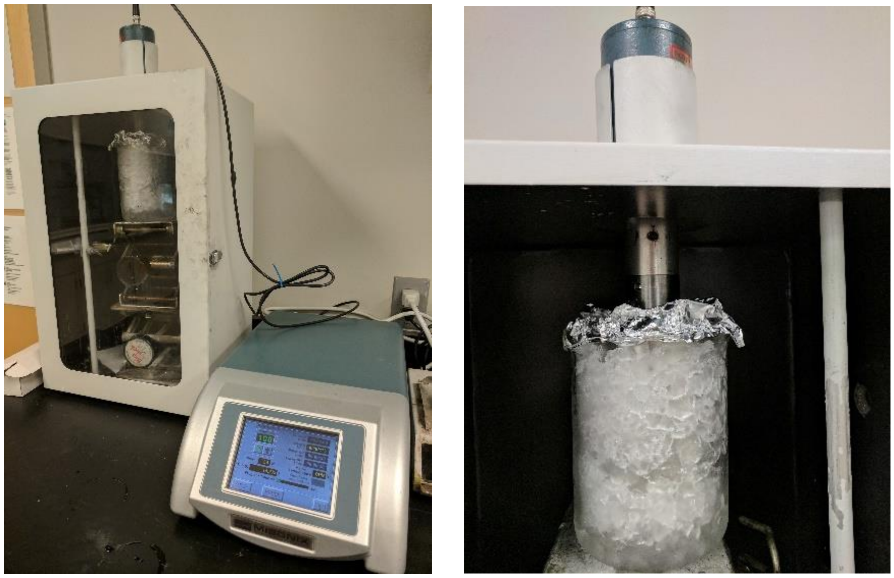

Figure 2 Ultrasonicate nanoplatelets with ice bath

High-speed disk (HSD) dispersers (high-speed impellers, high-intensity mixers) was used in the second method to break down the particles by providing shear stress during the dispersion process, as shown in *Figure 3*. All test samples were illustrated in Fig. 4.

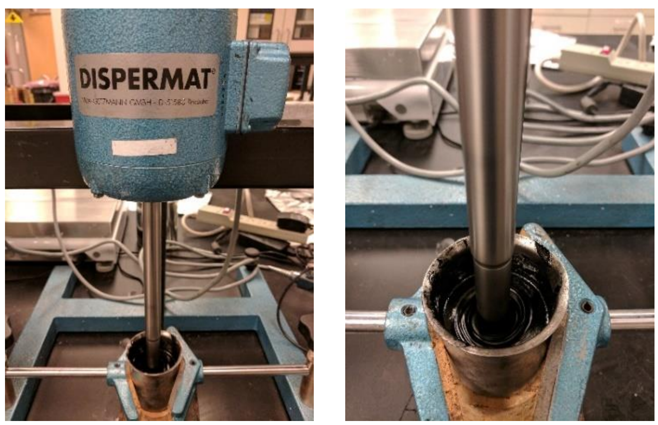

Figure 3 High-speed disk (HSD) dispersers

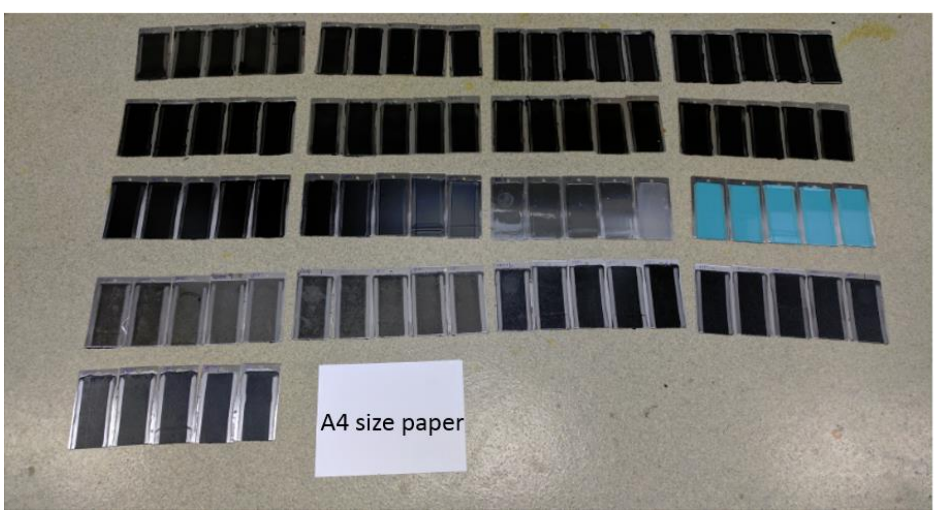

Figure 4 Coated test panels

2.2 Characterization of nano-modified coating

For a better understanding, the corrosion resistance behaviors of the coating were evaluated at various periods of time using EIS tests under Salt Fog test (ASTM B117). Potentiostatic EIS test was planned to be performed on each sample before the salt fog test, 24 hrs., 200 hrs. and 500 hrs. after the salt fog test.

2.2.1. EIS test

As discussed in the second quarterly report, EIS test is used to evaluate the interface properties between a substrate and conductive electrolyte solution which the applications can be coating performance evaluation.

2.2.2. Salt Fog Corrosion Test

The ASTM B117, Salt Fog test, is an accelerated corrosion test which the samples are exposed to a corrosive environment in a fog chamber. The samples are required to be maintained in a salt fog test environment during the test, and the salt solution should be 5% NaCl solution with a PH ranged in 6.5 to 7.2. The temperature should be maintained at 35°C (95°F).


Figure 5 Scribing coated sample with engraving machine

The test specimens should be suitably cleaned before placing into the chamber. Base on the ASTM B1654, to determine the development of corrosion from an abraded area in the coating, two scribed lines shall be made through the coating like showing in Fig. 5. To protect the uncoated metallic surface in the panel, we have used 3M™ Polyester Tape 8992L to cover these areas and the back of the panel. Sufficient pressure should be being applied by thumb and wood stick (Fig. 6) to make sure the tape is well-glued to the panel. Otherwise, the salt solution will be able to get into the uncoated area during the test. For the area without scribed lines, EIS test can be applied to evaluate the performance of the coating under the corrosive environment (Fig. 7).

The salt fog chamber and tested samples are shown in Fig. 8. After exposure, the surface of the coated sample should be cleaned by following ASTM B1654. All the corrosion products should be removed along scribe lines by either scraping, knife, paint stripper, air blow-off or power washer. Then the sample can be evaluated based on the defected areas by following the rating method from B1654.

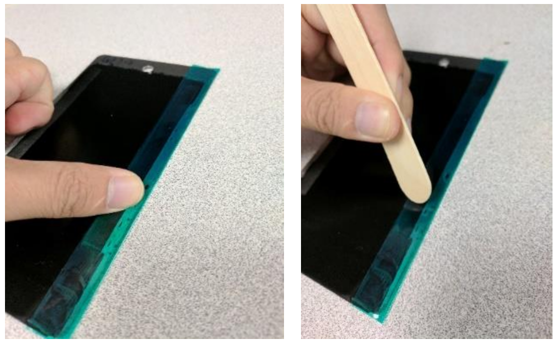

Figure 6 Prepared test sample for Salt Fog test

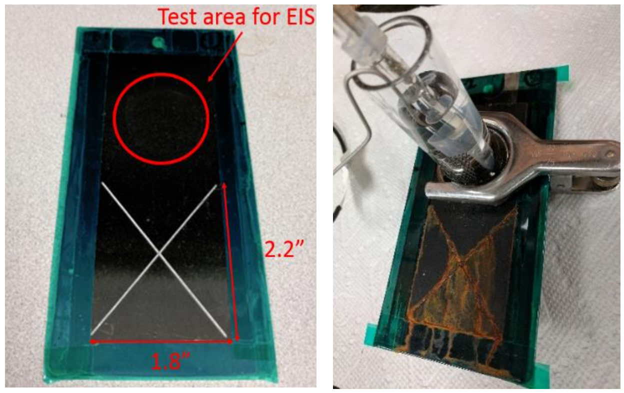

Figure 7 Incorporating EIS test on a prepared sample

Figure 8 Salt Fog Chamber with tested samples

2.3 Results and discussions

This section is to discuss the EIS results before salt fog test, 24 hrs. and 200 hrs. after the salt fog test, where the tendency of the corrosion behavior of each sample group can be observed.

2.3.1. Effects of the nanoparticle dosage on the coating performance

The impedance curves of graphene/epoxy composites which mixed by the second method are shown in Figs. 9 and 10. The nano-modified coatings exhibit higher impedance modulus over control samples at all time. After 200 hours of Salt Fog test, unlike the pure epoxy samples, most of the nano-modified coated samples only have slightly change.

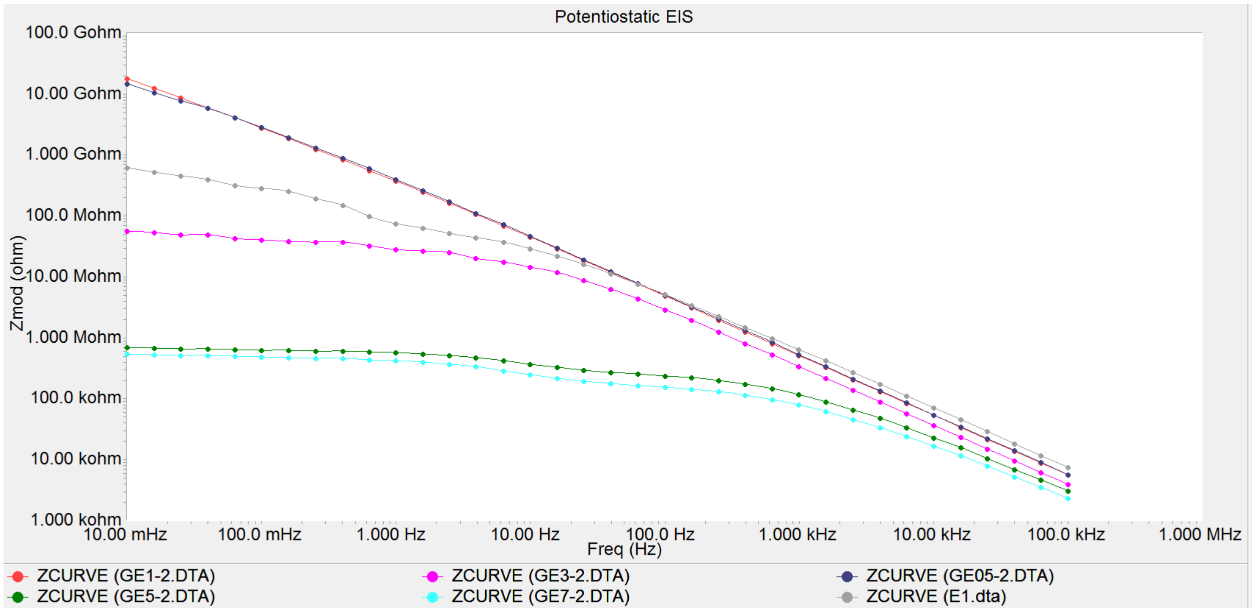

Figure 9 Initial impedance modulus for the coating (dispersion method 2)

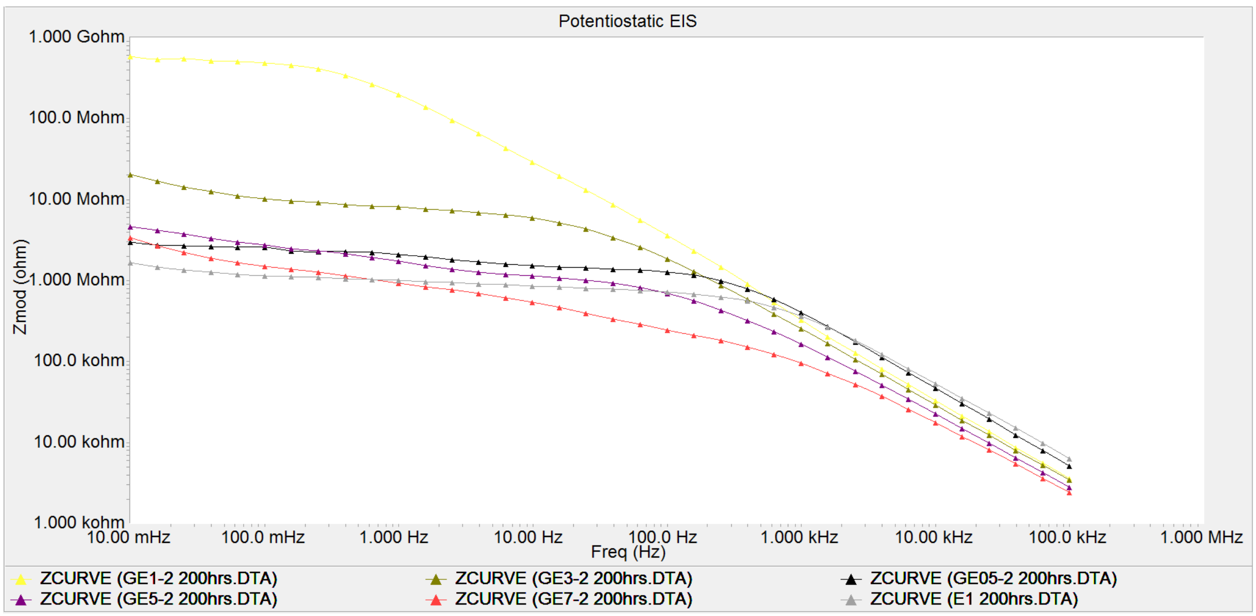

Figure 10 Impedance modulus for the coating after 200 hours Salt Fog test (dispersion method 2)

2.3.2. Effects of the dispersion methods on the coating performance

In addition, it can be easily observed that the dispersion methods can significantly affect the performance of the coating. Fig. 11 shows the Zmod values were mixed by the method 1 and method 2. The plots show that the sample that mixed by the method 2 has significantly higher corrosion resistance than the sample that mixed by the method 1. The results indicate the method 2 (with HSD disperser) can disperse nanoparticles more effectively compare with method 1.

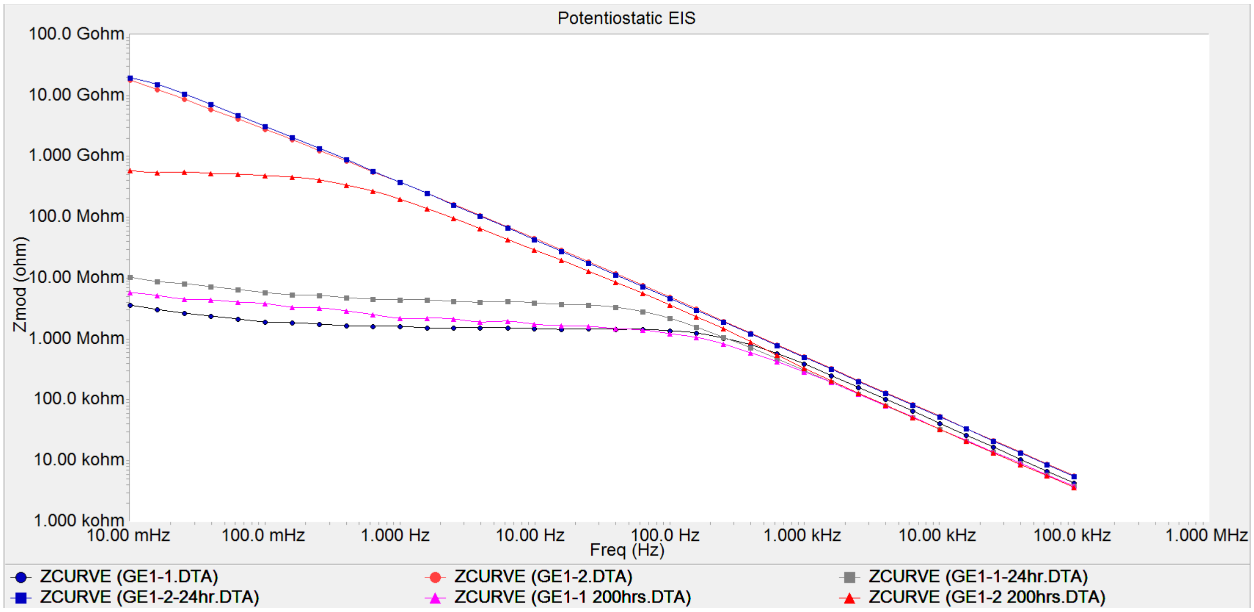

Figure 11 Impedance modulus of the coating with 1 wt.% of graphene under two methods

2.4 Dissemination of project results

2.4.1. Internationally Invited Talk

The PI Dr. Lin has several internationally invited talks in this summer by four international universities: China University of Mining and Technology, Beijing, China; Nanchang University, Nanchang, China; Nanchang Institute of Technology, Nanchang, China; and Jinggangshan University, Jian, China, for the dissemination of the latest research results through the seminars. These activities not only could contribute to the public awareness of the coatings, oil and gas pipelines, but also educate next-generation civil engineers who will pursue this area in their future career.

Figure 12 Dissemination of the research in the invited talks

2.4.2. High school student outreach program

In this summer, two high school female students from North Dakota Governor's Schools program were invited to have five-week to experience the research in our research group. This outreach will be unique for us to disseminate our research and foster the next-generation engineers to gain better understanding of the science and material, and could motivate them to pursue this area in their future career.

This outreach will continue till the middle of this July. The Students were paired with our group based on their interest. During these weeks, students will gain ideas of the corrosion behaviors of metallic materials and conduct experiments in the lab. We will document these activities and outcomes in the following report.

(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:

- Characterize and optimize the nano-modified coatings as identified,
- Optimize the new coatings through three aspects, and
- Summarize the findings of the survey (tentative) and draft the journal paper(s).