CAAP Quarterly Report

Date of Report: *Mar. 31st, 2020*

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

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For quarterly period ending: *Mar. 31st, 2020*

Business and Activity Section

(a) Generated Commitments

Ongoing invited keynote speech: Dr. Lin is invited and will give a keynote speech, "*Nano-modified Functional Coatings for Pipeline Corrosion Control*", on *Global Conference on Metallurgical Coatings and Thin Film*, Aug. 03-04, San Antonio, USA.

Top journal paper published: a journal paper, entitled "*Machine learning-enriched Lamb wave approaches for automated damage detection*" was published in a top Journal - Nanomaterials (Impact factor=3.031). PhD student Xingyu Wang who mainly takes charge of this research was one of major authors.

Two manuscripts were submitted to Top Journal- Composites Part B-Engineering (Impact factor=6.864), entitled "*Nano-Modified Functional Composite Coatings for Metallic Structures: Part I-*

Electrochemical and Barrier Behavior" and "*Nano-Modified Functional Composite Coatings for Metallic Structures: Part II- Mechanical and Damage Tolerance*". PhD student Xingyu Wang who mainly takes charge of this research was the first author.

One manuscript was submitted to Top Journal- Nanomaterials (Impact factor=4.034), entitled "*Comparative study of carbon nanotubes, graphene, and fullerene C60 additives for enhanced carbon-based polymer nanocomposites*". PhD student Xingyu Wang who mainly takes charge of this research was the first author.

(b) Status Update of Past Quarter Activities

The research activities in the 14th quarter included: (i) Long-term performance of the proposed high-performance nano-modified coating; (ii) Appearance and viscosity of nanocomposites; (iii) Defect observation associated with different nanocomposite coatings, as summarized below.

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

14.1 Objectives in the 14th Quarter

The high-performance nano-modified coating has been developed. The characterization and performance of the coating have also been well studied, which has excellent corrosion resistance, mechanical properties, and superior hydrophobicity, with outstanding durability. At that point, the authors have already achieved all the proposed ideas in the project proposal.

Besides physical and chemical properties, the authors would like to further investigate the mechanism of nanofiller reinforcement. Until recent, most of literatures and experiment studies have proved that the addition of nanofillers can provide positive effects in the polymer performance; however, it is still lack of study to understand the mechanism of nanofiller reinforcement. To address this gap, several cutting-edge techniques have been applied to characterize the nanofiller reinforcement in this project, such as transmission electron microscopy (TEM), scanning electron microscope (SEM), atomic force microscope (AFM), nanoparticle size distribution (PSD), Fourier-transform infrared spectroscopy (FTIR), and X-ray powder diffraction (XRD). In this report, the authors have further investigated the mechanism of the nanofiller reinforcement in the polymer matrix.

14.2 Experiment design

14.2.1 Experimental objectives

The plan of the experimental study included:

i. To further investigate the durability of the multifunctional coatings, salt spray exposure was continued, and the corrosion resistance and hydrophobicity were evaluated after exposure.
ii. In addition, the appearance and viscosity of nanofiller/epoxy matrixes was examined to characterize the nanocomposites.

The detailed results and discussions were presented in the following sections. For the test methods that have been applied in the previous study, the procedure was used without any changes in this report.

14.2.2 Durability test of the nanocomposite coatings

Salt spray test (ASTM B117) was applied as an accelerated durability test, where the specimens were exposed to salt fog spray with evaluated temperature in a Q-Fog CCT chamber for exposure hours, and EIS measurements were conducted before and after the exposure periods. With such, the developed nanocomposite coatings were evaluated using the results and their long-term performance were then assessed.

14.2.3 Viscosity of nanofiller/polymer mixture

To evaluate the influence of nanofillers on the rheological properties of the polymer matrix, viscosity test was performed after nanofillers were dispersed into epoxy resin, with a Brookfield DV-II viscometer (Figure 1). The experiment was conducted under room temperature (23°C), and #7 spindle were selected, while the rotational speed was 50 rpm.

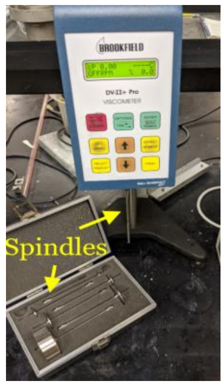

Figure 1. Brookfield DV-II viscometer for viscosity test

14.2 Results and Discussion

14.3.1 Durability evaluation of the proposed high-performance multifunctional coating

To further evaluate the durability and reliability of the proposed high-performance nanomodified coating. The specimens were continuously exposed to the salt fog spray, and the exposure time has increased to 2000 hours. The results for corrosion resistance, hydrophobicity, and water repellency were summarized below.

14.3.1.1 Corrosion barrier performance after exposure: EIS

The impedance and phase angle plots for the proposed coatings were illustrated in Figure 2, no degradation on corrosion resistance of the coating was observed during the entire 2000 hours exposure time. The coating behaved as an intact protective film as a straight line was observed in impedance curve and the phase angle was around -90 degrees in over a wide frequency region. As expected, the results confirmed the proposed coating has extraordinary anti-corrosion performance and durability.

14.3.1.2 Hydrophobicity after exposure: contact/sliding angle

The stability of the hydrophobic surface on the developed coating was further examined by measuring the contact angle after salt fog spray. No significant changes were observed for 1000 hours exposure, indicating that the properties successfully against the severe environment.

14.3.1.3 Water droplet adhesion after exposure

The coating surface has excellent water repellency which water droplet was easily detached from the surface during the test. The results from the water adhesion showed a strong agreement with the contact angle test.

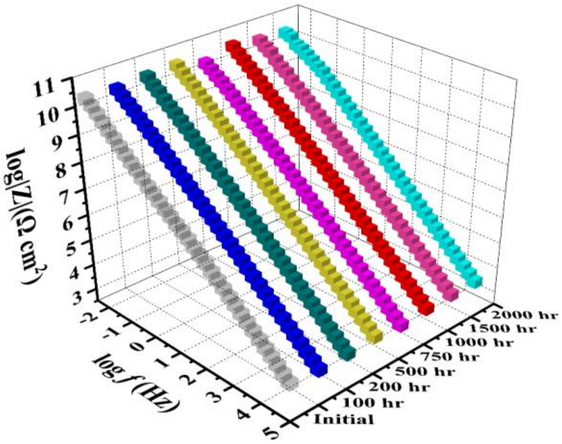

Figure 2. Impedance curve of the coatings

14.3.2 Viscosity and appearance of the nanofiller/polymer mixtures

The obtained results from the viscosity test and color appearance were summarized in this section, and the discussion was made based on the results.

14.3.2.1 Neat epoxy

The Epon 828 is an undiluted clear polymer liquid epoxy resin, as shown in Figure 3. The neat epoxy resin has a viscosity of 21440 cP at 23°C. It is well known that the viscosity of polymers can be varied by different temperature and set-up parameters of the viscometer, so all the tests were performed under the same condition in this study.

Figure 3. Neat epoxy resin

14.3.2.2 Single filler/epoxy mixtures

The nanofiller/epoxy mixtures that containing CNT, GNP, and NS nanoparticles were shown in Figure 4, respectively. The color of epoxy was changed to dark color with even a small amount of CNT and GNP nanofillers. For the NS/epoxy nanocomposites, the sample of NS has a dark brown color and reduced transparency, compared with the pure epoxy.

(a) (b) (c)

Figure 4. Appearance of (a) CNT/Epoxy, (b) GNP/Epoxy, and (c) NS/Epoxy mixtures

The viscosity values of single filler/epoxy mixtures were summarized. In general, small amount of nanofillers (0.1wt.%) has slightly reduced the viscosity of epoxy resin, and the vicosity was increased by higher amount of nanofillers, and could be higher than the pure epoxy.

14.4 Summary

In this report, we presented the test results from the experiments study that proposed from the last report, which includes:

1. Long-term performance of the proposed high-performance nano-modified coating
2. Appearance and viscosity of nanocomposites

The detailed results were presented in the previous section, and the findings were summarized and discussed below:

1. Long-term performance of proposed high-performance nano-modified coating:

   The proposed multifunctional coating has maintained its protective properties after 2000 hours of salt spray exposure. Based on the EIS results, the coating film was still intact after salt spray as no degradation was observed. In addition, as high contact angle and excellent repellency for both water and the organic liquid was maintained.

2. Appearance and viscosity of nanocomposites:
   - I. With a small amount of CNT and GNP nanofillers, the color of epoxy changed to dark color
   - II. The sample with 0.1wt.% of NS has a dark brown color and reduced transparency, compared with the pure epoxy. And the transparency was continuously decreased, and the color changed to light brown when higher content of NS was added.

(e) Description of any Problems/Challenges

No problems are experienced during this report period

(f) Planned Activities for the Next Quarter

The planned activities for next quarter are listed below:

- To further investigate the long-term performance of the multifunctional coating, the exposure duration will be extended.
- Data analysis for correlation study between defect analysis and coating performance.