CAAP Annual Report

Date of Report: *Oct 9, 2015*

Contract Number: *DTPH5614HCAP05*

Prepared for: *DOT and PHMSA*

Project Title: *Improved Coatings for Pipelines*

Prepared by: *Texas Engineering Experimental Station*

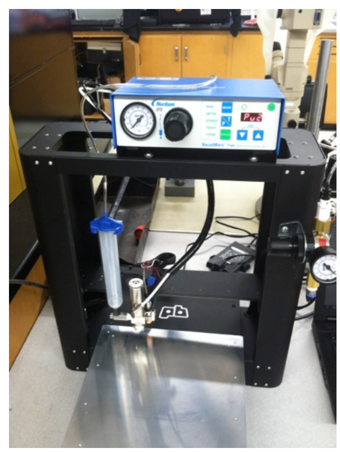
Contact Information: *Dr. H. –J. Sue, 1-979-845-5024, hjsue@tamu.edu*

For annual period ending: *September 30, 2015*

Business and Activity Section

1. Generated Commitments -

In addition to holding 5 meetings we have met with the Pipeline Research Council International in Houston, Texas, to briefly discuss this project with PRCI leadership. We have tentative plans to present this project to PRCI membership at a technical meeting. Our primary goal for these discussions is to gather additional input in order to maximize our chances of developing a new technology that is commercially successful.



Our existing partners (Dow Chemical and Shawcor Ltd.) have the capabilities we need to complete our milestones. Dow Chemical has provided raw materials and formulation advice. Shawcor has shipped several batches of test panels and has run tests on our coatings, in addition to offering invaluable information on coatings for the pipeline market.

We have successfully developed a 'spray robot' that will allow us to improve the reproducibility of our coatings to improve the precision of our test data (see image at right). More detail is in the 'Status' section.

2. Status Update of Past Year Activities -

Summary of coating test results

We have been gratified to discover that our postulated improvements in coatings properties from well-exfoliated nanoplatelets have largely been realized. Although nanoplatelet-filled coatings have been reported in the past, the improvements compared to conventional fillers were modest.

Note that there are several technical problems to overcome before our coatings can be used commercially. These are delineated in the 'Problems / challenges' section below. Nevertheless, we have proven for the first time that significant improvements in scratch resistance and corrosion protection are possible with nanoplatelet fillers.

We have been applying a thin (50-100 µm) overcoat of our nanofilled formulation on top of a proprietary epoxy coating that Shawcor applies to steel panels. An initial concern was adhesion between our overcoat and the Shawcor coating. Results from scratch tests at Texas A&M have shown that the adhesion between the coatings is excellent. In addition, 28 day boiling water immersion tests at Shawcor have similarly shown good adhesion.

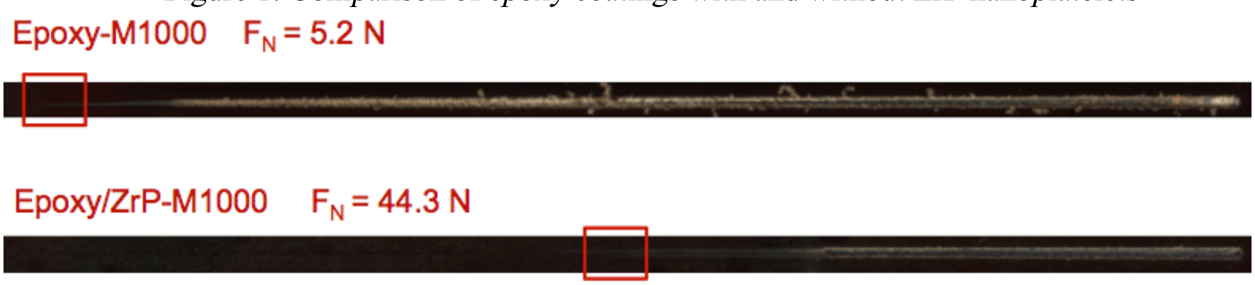
Our results from cathodic disbondment tests at Shawcor have been mixed. Our preliminary tests using D.E.H. 615 (aliphatic amine) as the hardener have shown improved results vs controls. More recent tests using Epicure W (aromatic amine) as the hardener did not give significantly different results.

Hot water immersion tests performed by Shawcor have shown that our coatings give improved results (‘adhesion rating’ from 1 to 2) that they deem significant. Dennis Wong from Shawcor attributes to the reduction in water diffusion rates through the coatings.

Coating scratch resistance measurements
During our most recent meeting, Fan Lei described her work related to measuring the scratch resistance of the coatings. Our scratch machine was used to compare formulation with and without ZrP nanofillers. Dramatic improvements were observed. Multiple tests show the results have low standard deviation.

In Figure 1 below, images from our laser confocal microscope of scratch surfaces for coatings prepared from the same formulation both with and without ZrP. The force on the tip increases from 1 to 100 N going from left to right. Red rectangles are used to highlight the areas where the onset of scratch visibility starts. The force required to cause visible damages increases from 5.2 to 44.3 N when ZrP is added, indicating significantly improved scratch resistance.

Figure 1: Comparison of epoxy coatings with and without ZrP nanoplatelets



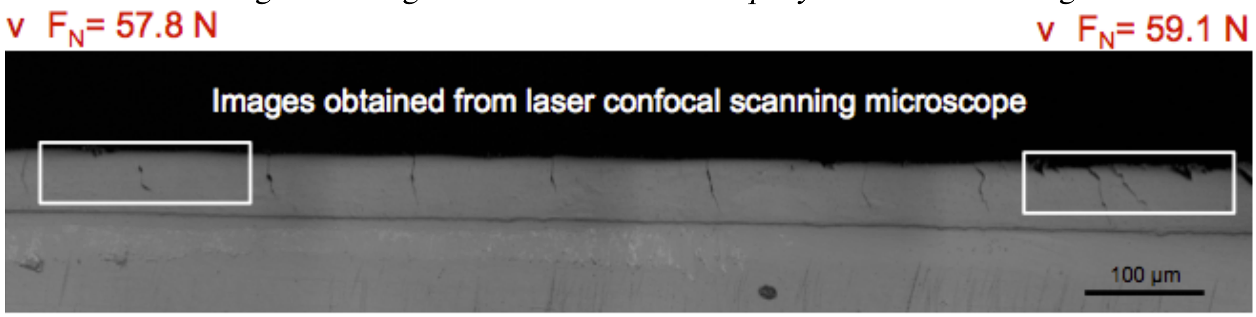
Notes: 1 mm spherical tip, 10 mm/s, normal load 1-100 N

The panels, precoated with a proprietary epoxy coating by Shawcor, were subjected to a heat-treatment using the same schedule as our ‘epoxy-M1000’ formulation. The purpose of this was to ensure that the properties of the ‘bulk’ coatings didn’t change after we added an additional coating and heat-treated it. When the ‘bulk’ coating was tested using the scratch machine using the same protocol shown in Figure 1, a visible scratch was observed starting at 10.2 N.

One concern that we discussed early in the project was adhesion between our nano-filled top-coat layers and the ‘bulk’ coating. We now have data that show that in the case of the epoxy/M1000 formulation, the adhesion is actually excellent.

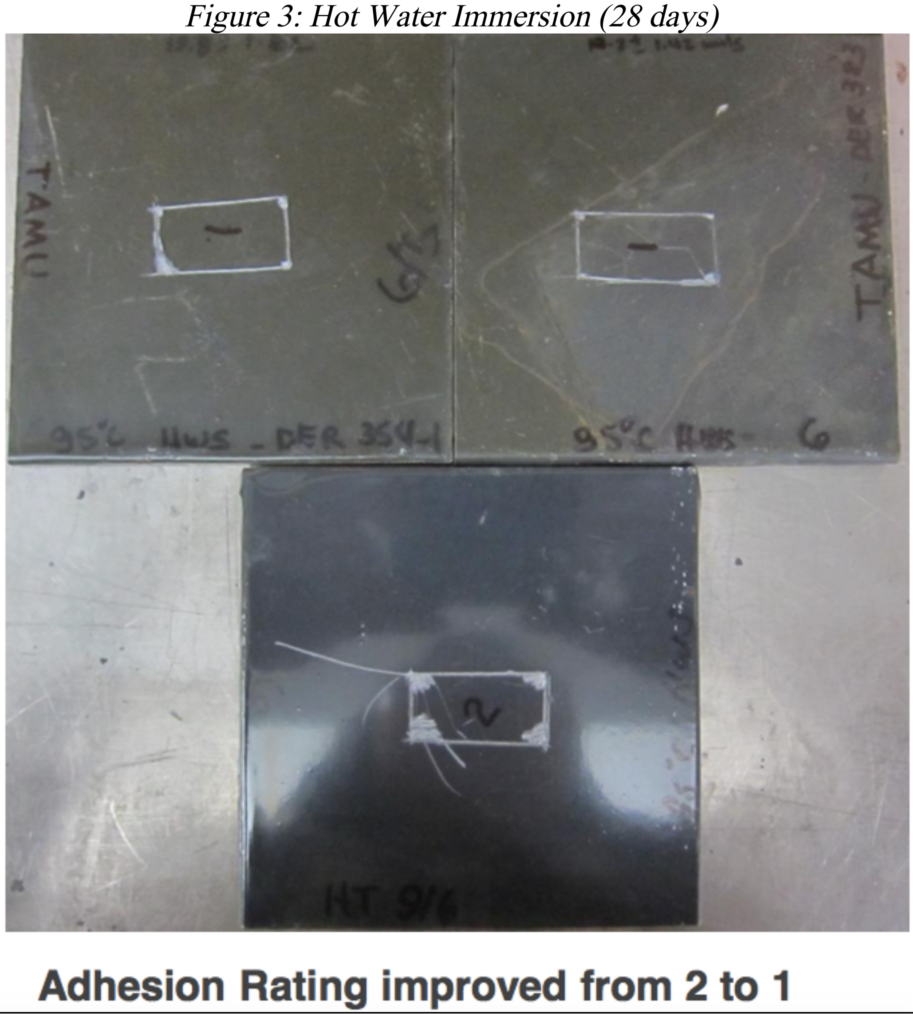
In Figure 2 an image taken of a vertical slice of the scratch is shown, specifically the portion of the scratch just after it is visible on the top surface. As the force increases from left to right, the crack density increases. Also note that there is adhesion between the epoxy/ZrP-M1000 top coat and the underlying ‘bulk’ coat is excellent. The cracks induced by the scratch tip do not propagate along the interface between the two coatings. In addition, images taken through cross-polarizers show that stress is induced in the ‘bulk’ coating, further showing the adhesion between the layers (see Fan’s presentation for more information: “20151005 DOT review.pdf”).

Figure 2: Image of vertical slide of the Epoxy/ZrP-M1000 coating



Cathodic disbondment test results
Dennis Wong discussed the new cathodic disbondment test results at room temperature, 50, 65, 80, and 95 ºC (see "Shawcor Overcoat test results 09-2015.doc"). In summary, there was not a significant difference between 'uncoated' samples and those over-coated with our epoxy/ZrP-M1000 coating. Dennis suggested that our coatings may not be sufficiently thick to see an effect. As a consequence, we will attempt to prepare thicker coatings (70-125 µm) and re-run the tests.

Figure 3: Hot Water Immersion (28 days)



Hot water immersion test results
Two separate series of test panels have shown that our ZrP overcoat improves the hot water immersion test results of Shawcor's proprietary coating (the most recent test results are shown

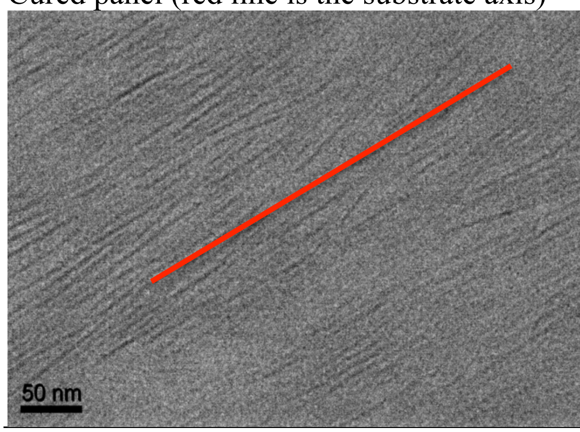
above in Figure 3). The two images at the top are two formulations that contain ZrP that have been over-coated onto Shawcor's proprietary epoxy coating. The image at the bottom is a panel that has not been overcoated. The two panels that have been overcoated show improved adhesion of the epoxy coating to the steel.

As Dennis explained, the water boil test is mostly a result of water diffusion through the coating. A reasonable hypothesis is that the ZrP nanoplatelets slow the rate of water diffusion, and improve the test results. The cathodic disbondment test is more complex, and 'holidays' play a role.

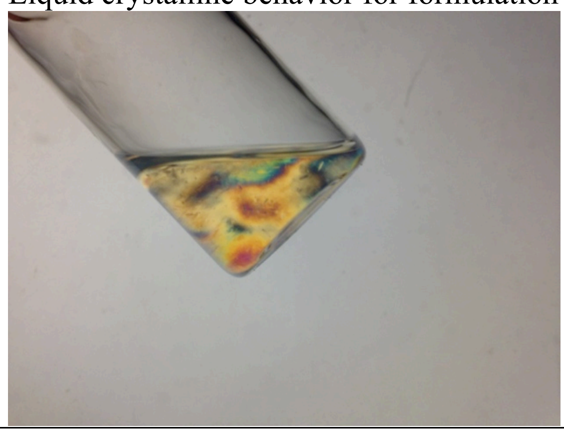
Characterization of coating morphology
Our hypothesized improvements in coating properties can only be realized if the nanoplatelets are fully exfoliated to achieve a high aspect ratio and the nanoplatelets are aligned parallel to the steel substrate. The image in Figure 4 (from transmission electron microscopy) at left shows that the exfoliation is not perfect, but it is quite good. The image (through crossed polarizers) at right is a glass vial containing the formulation before coating. The ability of the formulation to rotate and diffract polarized light shows that the nanoplatelets exhibit significant alignment before application and cure. This optical behavior is characteristic of liquid crystalline materials.

Figure 4: TEM (left) and photograph in polarized light (right) of ZrP/D.E.R.383 with D.E.H. 615

Cured panel (red line is the substrate axis)



Liquid crystalline behavior for formulation



Spray robot
Our initial coatings were applied using a small hand-sprayer. Although this gives acceptable results, we felt that we needed a method that would give better precision. Our thought was to purchase an inexpensive 3D printer, modify it, and attach a high quality spray head. This has proven to be successful. We spent ~$5,000 total for parts to build the spray robot. The applications written for 3D printing were not useful for our purposes, and so we developed our own. We are able to adjust the spray pattern, speed on both axes, number of layers, and other parameters.

There are also numerous spray-head parameters that can be adjusted that affect the quality of the coatings, including the nozzle dimensions, liquid pressure and flow, the atomizing air pressure, and others. This required considerable time to optimize, but we are now able to prepare reproducible coatings of good quality. We are able to achieve an average surface roughness for our epoxy/ZrP-M1000 coatings of 1 μm, which both Dow and Shawcor have said is adequate.

One persistent problem is circular defects in the coatings that are likely due to the escape of trapped solvent that remains before cure. The concentration of these defects is not so high that the coated panels can't be tested. Nevertheless, we are attacking this problem in several ways. We have modified our cure schedule to allow for more time for acetone evaporation prior to cure. We are adding a heated platen to our spray robot so that solvent can evaporate at a faster rate as the coatings are applied. Finally, we are reducing the amount of solvents in our formulations. The ultimate solution to this problem is to avoid solvents entirely. One of the action items for this quarter is to investigate the rheology of the neat formulation to determine whether our spray robot can handle them. Our industrial partners have made it clear that solvents are not desirable for commercial applications.

3. Description of any Problems/Challenges -

Two items were discussed during the meeting this quarter.

1. The improvements in cathodic disbondment test results that we observed previously were not seem in the most recent series of tests. Dennis suggested that we need thicker over-coats. We will attempt to test this hypothesis in the upcoming quarter.
2. As was discussed previously, for commercial application we will need to eliminate solvents from our formulation. We will gather some viscosity data to determine whether this is possible with our current formulation. Note that developing a commercial coating is beyond the scope of this project.

Two items from previous quarterly reports have not been completely resolved. Neither issue has prevented us from achieving the project goals, but both will need to be resolved before the technology can be commercialized.

1. Our ZrP-containing formulations are unstable when aliphatic amine hardeners are used. Aliphatic hardeners are commonly used to achieve fast cure at temperature below 100 ºC. We have not truly resolved this problem, although we are able to circumvent it in the lab by cooling the formulations and working quickly. Another option is to use an aromatic amine hardener, which is unfortunately less reactive.
2. Scaleup of the ZrP nanoplatelets has been resolved on a lab scale. The use of thin 'overcoats' for testing has helped reduce the amount of ZrP that we need for testing.

4. Planned Activities for the Next Quarter

1. Re-run the cathodic disbondment tests with thicker overcoats. Shawcor will determine how many panels we need for the tests and ship them to us. We will overcoat the samples and ship them back for testing.
2. We will use X-ray diffraction to measure the orientation of the nano-platelets in the coatings. This is to address a concern that there will be a tendency for the nano-platelets to have random orientation as the coating thickness increases.
3. We will measure neat (no solvent) viscosities of our epoxy/ZrP-M1000 formulation to determine whether it is possible to avoid solvent.

Appendix

Meeting notes for DTPH5614HCAP05 (Improved Coating for Pipelines)

05-Oct-2015 at Texas A&M in College Station, TX

Phone Attendees:

- DOT - PHMSA: Jay Prothro
- Dow Chemical Co.: Rajesh Turakhia, Lingyun He
- Shawcor Ltd: Dennis Wong, Catherine Lam
- Texas A&M: Prof. Hung-Jue Sue, Fan Lei, Peng Li, Michael Mullins

Presentations:

- Fan gave a presentation on technical progress: "20151005 DOT review.pdf"
- Dennis discussed Shawcor's test panel test results "Shawcor Overcoat test results 09-2015.doc"

Notes (items in italics are action items):

- Fan Lei presentation
  - Spray robot optimization
  - Surface roughness of 1.075 µm for the coatings has been achieved. Both Dow and Shawcor said this was adequate
  - Fan discussed the experimental parameter for the scratch test
  - The 'Standard Coefficient of Friction' was substantially lower for the ZrP overcoated samples. The low SCOF persists until ~50 N is reached, which corresponds with the first observable damage from the laser confocal microscope images.
  - The force required for first visual damage to the coating is ~10x higher (44.3 vs 5.2 N) for the epoxy/ZrP-M1000 samples vs the epoxy/M1000 control.
  - An image from the side of the scratch surface for a ZrP sample taken at the first point where damage is observed shows cracks through the overcoat do not propagate along the surface, suggesting strong adhesion between the overcoat and Shawcor's epoxy coating.
- Dennis Wong (Shawcor) discussion of data:
  - There were no significant differences between the overcoated samples and the non-overcoated controls.
  - He suggested that our overcoats were too thin, and we should try to achieve 75-125 µm thickness

Plans for next quarter: see Section 4 above.

September 25, 2015

Dr. Hung-Jue Sue
Texas A&M University
College Station, TX 77843-3123
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RE: 4th quarter industrial support for DOT pipeline project DTPH5614HCAP05

Dear Dr. Sue:

Our 4th quarter support for the quarter for staff time, expenses, and materials is $5188.02. A breakdown of this total is shown below.

Project Activity	**Contributed Cost in $**
Staff time for coating formulation, testing, evaluation, meetings	2100
Materials, sample preparation, consulting	
Travel expenses	3088.02
Total	5188.02

Sincerely,

Dennis Wong, PhD, P Eng
Technology Group Manager, Coatings
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dwong@shawcor.com

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DATE: 10/8/2015

Dr. Hung-Jue Sue
Texas A&M University
College Station, TX 77843-3123
+1 979 845 5024

RE: 4th quarter industrial support for DOT pipeline project DTPH5614HCAP05

Dear Dr. Sue:

Our 4th quarter support for the quarter for staff time, expenses, and materials is $2140.44. A breakdown of this total is shown below.

Project Activity	**Contributed Cost in $**
Staff time for coating formulation, testing, evaluation, meetings	621.46
Laboratory overhead and admin. services expense	1518.98
Materials, sample preparation, consulting	0.00
Travel expenses	0.00
Total	2140.44

Sincerely,

Lingyun He