# CAAP Quarterly Report

Date of Report: *January 8, 2016*

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 quarterly period ending: *December 31, 2015*

## Business and Activity Section

**1. Generated Commitments -**

There have been no additional teaming agreements.

We had a phone meeting with representatives from the DOT, Shawcor, and Olin (was Dow Chemical) on January 7th, 2016. The notes are included in the Appendix.

**2. Status Update of Past Quarter Activities -**

Here is the list of plans from the previous quarterly report.

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.

Items 1 and 3 were completed (see detailed discussion below), but item #2 related to X-ray diffraction was not. We will try to get this done next quarter.

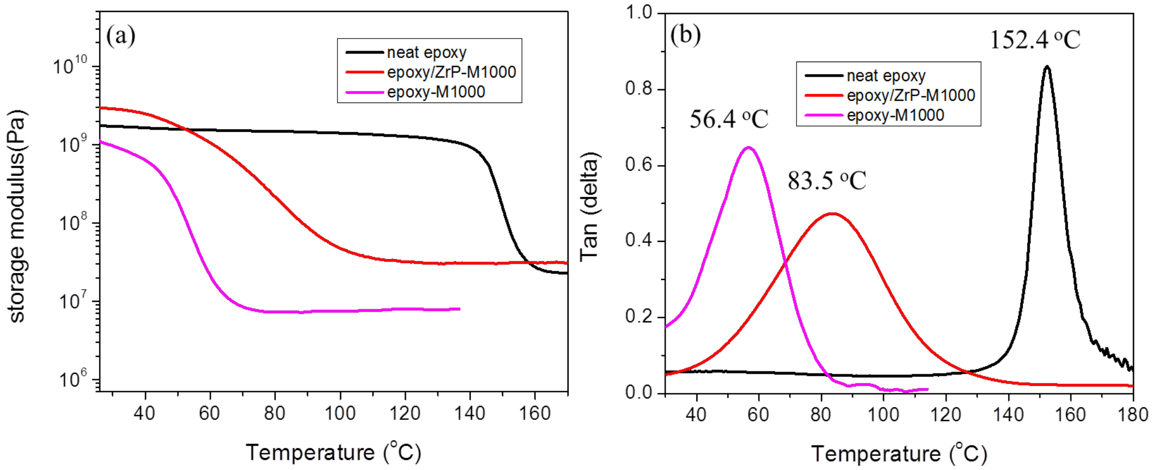
*Sample shipments from Texas A&M*

11/30/15: Five 4”x12” green steel panels with topcoat thickness of 75 µm.
12/16/15: Eight 4”x4” panels with topcoat thicknesses of 50 µm and 100 µm.
Three 4”x12” panels with topcoat thickness of 50 µm
One 4”x12” with topcoat thickness of 100 µm.

*Experimental results from Texas A&M*

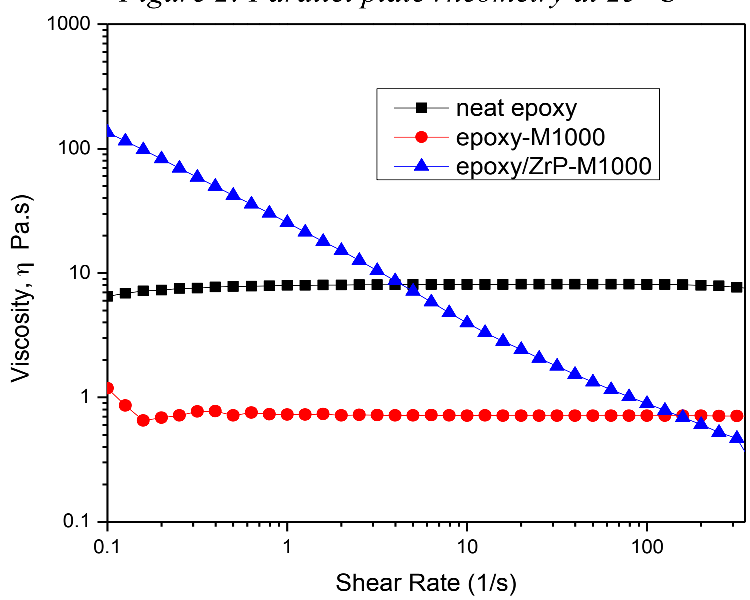
Free-standing films were prepared and tested with a dynamical mechanical analyzer (see Figure 1). Three formulations were used: 'neat' epoxy (D.E.R.™ 354 cured with the aromatic hardener DETDA); 'neat' formulation with 16% Jeffamine™ M1000; 'neat' formulation with 10% ZrP. The Tg's of the 3 formulations are 152.4, 83.5, and 56.4 ºC, respectively.

*Figure 1: DMA tests for free-standing thin films*




We have mixed acetone with the formulations to produce thin coatings from the spray process. Although this works well in the lab, it is not practical in the field. The apparent viscosity of the formulation with ZrP is quite viscous, but we were hopeful that the high shear produced during the spray process might drop the viscosity enough for spraying. Parallel plate rheometry was run (see Figure 2) on the three formulations. The effect of the nano-platelets on the viscosity vs shear curve is dramatic (see blue curve in Figure 2).

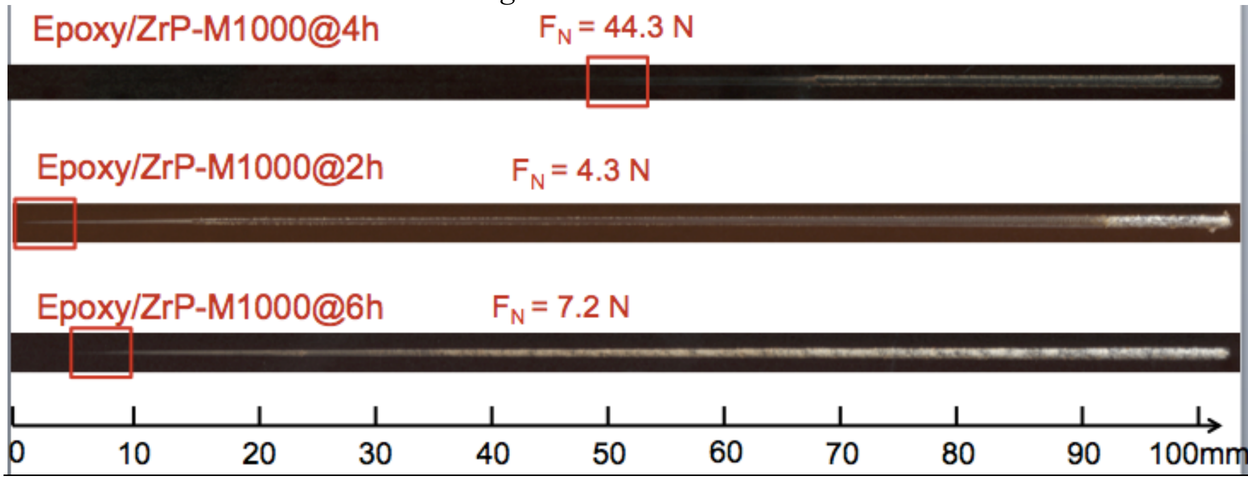
*Figure 2: Parallel plate rheometry at 25 ºC*




We attempted to spray the ZrP/M1000 formulation without solvent. Unfortunately, rough coatings are produced. We suspect that this is because the spray droplets don't flatten sufficiently after hitting the panel. Because the low-shear viscosity of the ZrP formulation is high, no 'leveling' occurs after spraying. We will try to improve this in the next quarter.

In past reports we described dramatically improved scratch resistance for coatings with ZrP. Fan showed some results from the scratch machine for coatings that were cured for various times at 200 ºC (see Figure 3). A cure time of 4 hours appears to be the optimum. However, this result may be due to slow rate of cure at 200 ºC and concurrent decomposition of the epoxy coating. We need to find a way to cure at lower temperatures, which is one of the plans for next quarter.

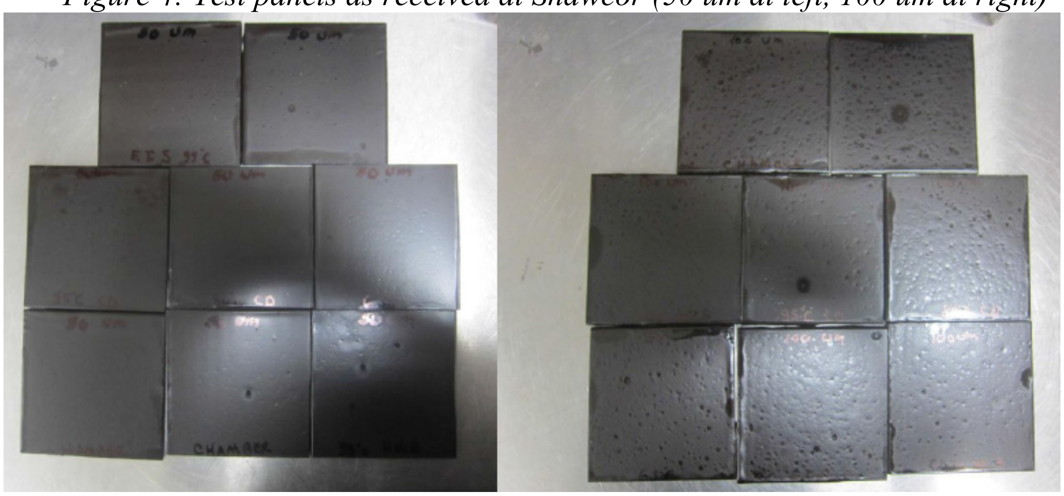
*Figure 3:Scratch test results*




*Shawcor experimental results*

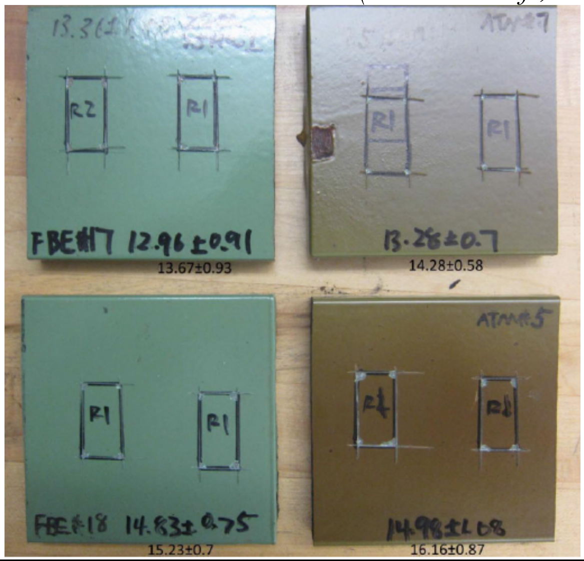
Catherine showed photos of the panels that were sent from Texas A&M (see Figure 4). These 'thick' coatings (50 and 100 µm) showed many 'craters'. Fan thought these craters were due to boiling of acetone. It is difficult in these thick coatings for acetone to diffuse through the nano-platelet layer. This is another reason that we need to work on avoiding the use of acetone for our spray formulations.

*Figure 4: Test panels as received at Shawcor (50 um at left, 100 um at right)*



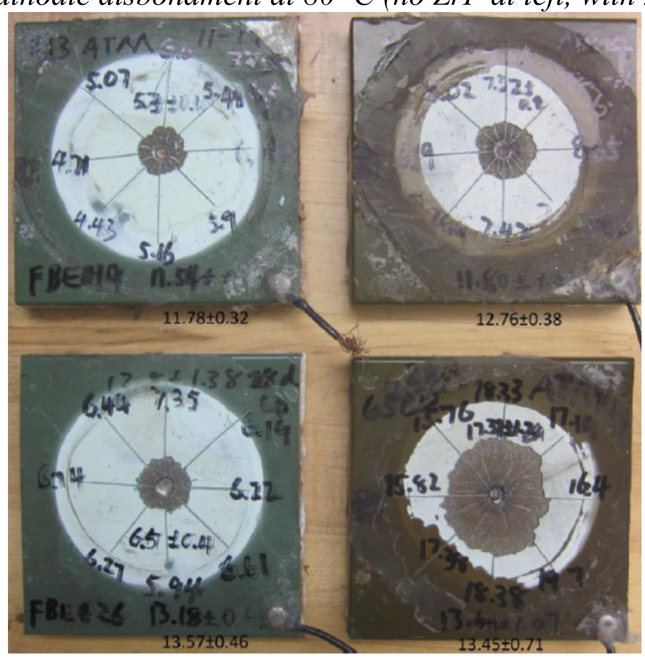
Catherine first described results from hot water immersion (HWI) tests (see Figure 5). Her interpretation is that there was no change between the samples coated with ZrP and those without coating. In the past we have seen improved results with ZrP. Note that the ZrP-coated samples were cured for 6 hours at 200 ºC, so this may explain the different results.

*Figure 5: Hot water immersion test results (no ZrP at left, with ZrP at right)*




Next Catherine described their cathodic disbondment test results (see Figure 6). In this case the samples overcoated with ZrP showed worse results. Again, we suspect this may be the result of decomposition of the overcoat and sub-coat during the 200 ºC for 6 hour cure process. Dennis said that their proprietary undercoat was not stable at these temperatures.

*Figure 6: Cathodic disbondment at 80 ºC (no ZrP at left, with ZrP at right)*




**3. Description of any Problems/Challenges -**

The biggest issues are the use of solvents (such as acetone) for spray formulations, and the need for high temperature cure (200 ºC) for the aromatic curing agent we are using.

**4. Planned Activities for the Next Quarter** -

- Understand and optimize the cure procedure with the goal of minimizing thermo-oxidative decomposition
- Reduce the number of craters in the 'thick' ZrP coatings
- X-ray measurements of morphology in the ZrP coatings.

<u>**Appendix**</u>

**Meeting notes for DTPH5614HCAP05 (Improved Coating for Pipelines)**

07-Jan-2016 phone meeting

Phone Attendees:

- DOT - PHMSA: Jay Prothro
- Olin (was Dow Chemical Co.): Rajesh Turakhia, Yong, Zhang, Lingyun He
- Shawcor Ltd: Dennis Wong, Catherine Lam
- Texas A&M: Fan Lei, Peng Li, Michael Mullins

Presentations:

- Mike Mullins gave a short introduction outlining deadlines
- Fan Li gave a presentation on technical progress: "DOT Fan Lei 2016-01-07 technical review.pdf"

Notes (items in italics are action items):

- Fan Lei presentation
  - After Fan showed the parallel plate rheometry data, Rajesh asked about viscosity 'recovery', which has an impact on coating quality. For example, if the scan from low to high shear was reversed, would the same trend be followed? Fan said she has some data that she didn't show.
  - Mike will follow up with Rajesh to see what rheology characteristics we need to have to improve our coating quality.
  - Fan showed DMA data (run at 1 Hz) showing Tg's for the 3 formulations: no additives 152.4 ºC; with ZrP(M1000) 83.5 ºC; with only M1000 56.4 ºC. The percentage of additives is 10 wt% for ZrP, 16 wt% M1000 with Epicure W (DETDA) as curing agent. Dennis said the Tg for the epoxy formulation with no additives seemed too high. Rajesh asked whether the film is fully cured at 120 ºC. Fan will run a DSC or other method to find out at what temperature the sample cures.
  - Dennis and Catherine thought the Tg might be too low, but Rajesh said they have passed the 80 ºC CD tests with coatings with Tg's ~ 50 ºC.
- Catherine Lam presentation
  - They received samples from TAMU ~Dec. 20, 2015. Results from these films will be finished in ~1 month. There were craters in both the 50 and 100 μm top-coated samples, with the thicker film being worse.
  - The results she showed were for their 'green' coating. The black coating results will be done in a few weeks.
  - HWI tests were run with tap water, 28 days at 75 ºC, not much difference
  - CD tests were not as good with ZrP top coat. Dennis said that hypochlorite and high pH forms during this test. Noticeable separation of the top coat was observed.
  - Fan said she cured the samples for 6 hours at 200 ºC. Dennis said the coatings probably degraded during this cure. We need to find a way to cure at lower temperature.
- Other discussions
  - Fan said she cured for 6 hours at 200 ºC because shorter times gave sticky coatings. We need to understand this.
  - Fan also said that when the neat coatings are sprayed that poor leveling occurs, in other words the spray droplets don't form a smooth coating when they hit the panel.

January 04, 2016

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

RE: 5th quarter industrial support for DOT pipeline project DTPH5614HCAP05

Dear Dr. Sue:

Our 5th quarter support for the quarter for staff time, expenses, and materials is $5144. A breakdown of this total is shown below.

| **Project Activity** | **Contributed Cost in $** |
|---|---|
| Staff time for coating formulation, testing, evaluation, meetings | 5144 |
| Materials, sample preparation, consulting | |
| Travel expenses | |
| Total | 5144 |

Sincerely,

Dennis Wong, PhD, P Eng
ShawCor Ltd
25 Bethridge Rd
Toronto
Ontario
M9W 1M7
+1 416 744 5807
dwong@shawcor.com