CAAP Quarterly Report

Date of Report: *July 9, 2015*

Contract Number: *DTPH5614HCAP05*

Prepared for: *DOT and PHMSA*

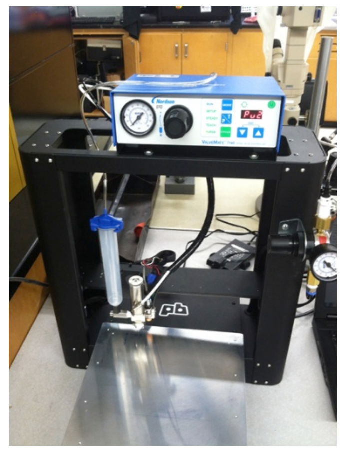
Project Title: *Improved Coatings for Pipelines*

Prepared by: *Texas Engineering Experimental Station*

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

For quarterly period ending: *June 30, 2015*

Business and Activity Section



1. Generated Commitments -

There have been no additional teaming agreements.

A 'spray robot' was designed, the parts were purchased and modified, and a control program was written. The cost of the parts was just under $5,000. Testing is underway, and so far the robot is working well. More details are included below.

We had a meeting with representatives from the DOT, Shawcor, and Dow Chemical on July 7th, 2015 at Freeport TX at Dow Chemical's site. 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.

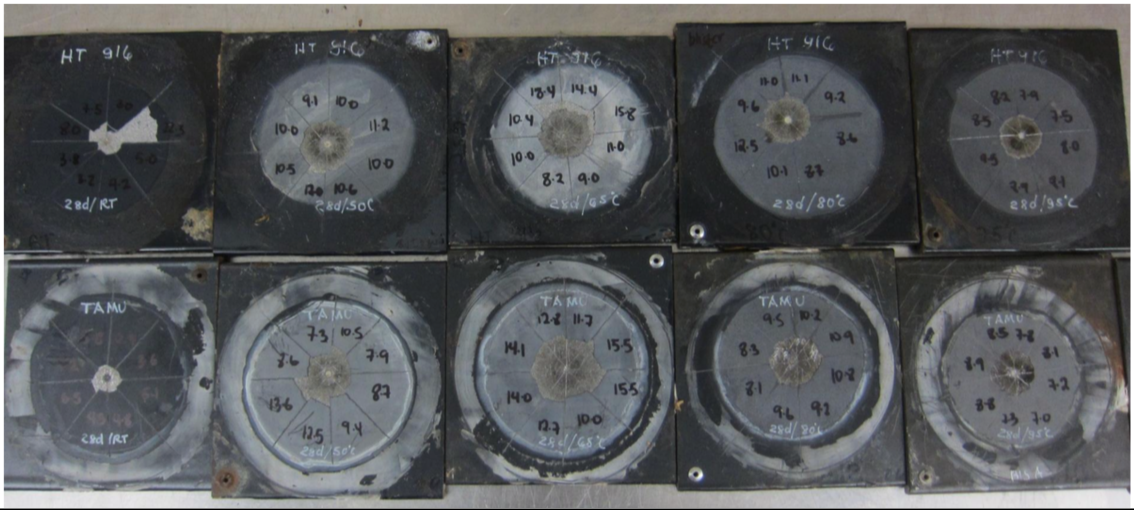
1. Shawcor will provide more panels for us to coat. We will run the EIS tests, and ship samples to back to Shawcor for them to run extended period testing.
2. We will work to develop formulations that can be cured at lower temperatures.
3. We are working on a 'robot-sprayer' that will improve coating thickness variation compared to our current manual process.

All of these items were completed (see detailed discussion below). However, additional work remains for items 2 and 3, and will carry over into the next quarter.

Plan item 1 (test panels)

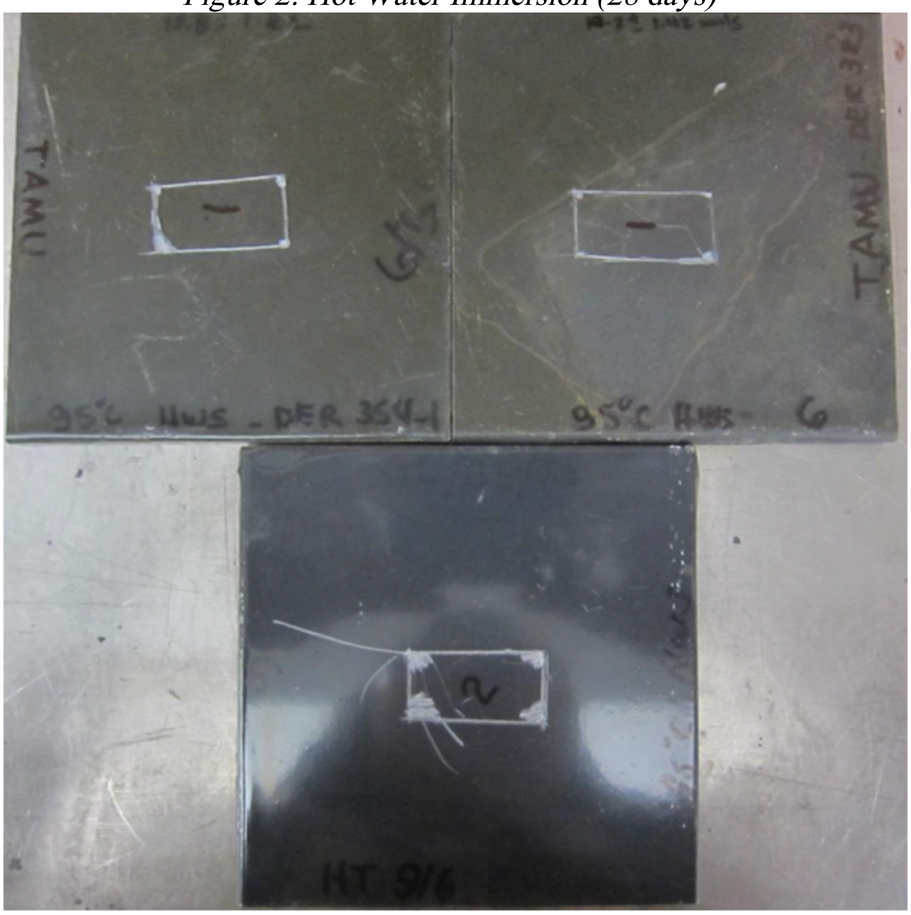
Steel panels pre-coated with a proprietary Shawcor formulation were coated with a 35 micron thick coating of ZrP-epoxy (D.E.R. 383) cured with D.E.H. 615 hardener. The panels were shipped to Shawcor. Two tests were run that compared control panels (no ZrP coating) with the panels coated with ZrP-epoxy). The first test was cathodic disbondment at 5 different temperatures (room temperature, 50, 65, 80, and 95 °C). In the room temperature test (see Figure 1), the ZrP-coated panel gave superior results. At the other temperatures (50 °C and above) the results were similar. This may be because the ZrP-epoxy coating Tg is near 50 °C (50 °C by DSC at a 10 °C/sec scan rate).

Figure 1: Cathodic disbondment at 5 temperature control (top) and with ZrP top coat (bottom)



In a second test (boiling water immersion for 28 days, see Figure 2), the ZrP-epoxy panel gave superior results. Note that this confirms the results obtained in the last quarter. 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 CD test is more complex, and 'holidays' play a role.

Figure 2: Hot Water Immersion (28 days)

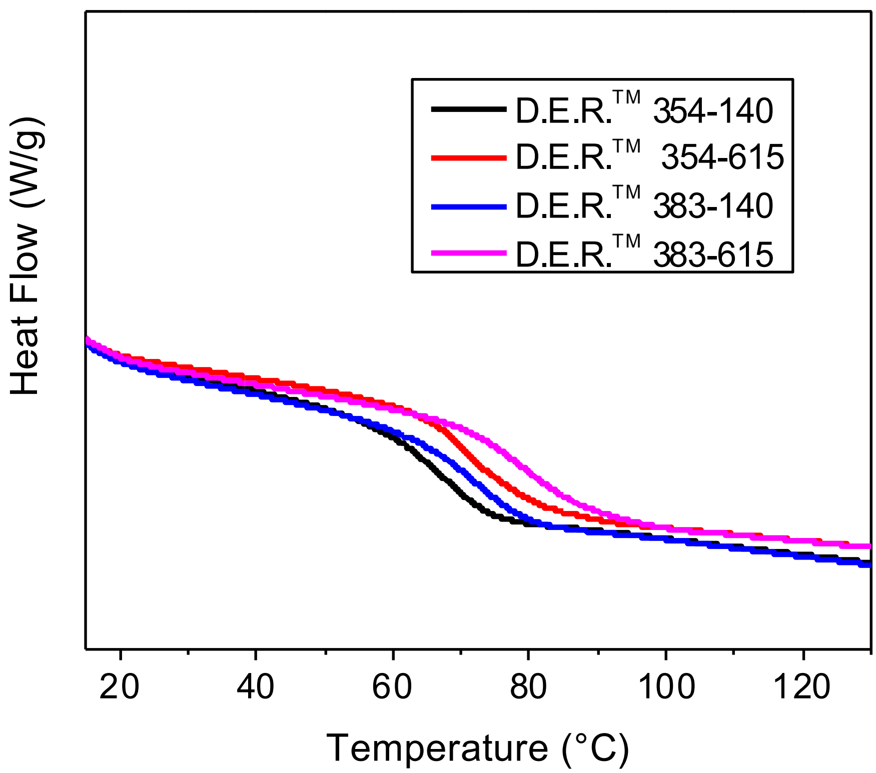


Adhesion Rating improved from 2 to 1

Plan item 2 (100 °C cure)

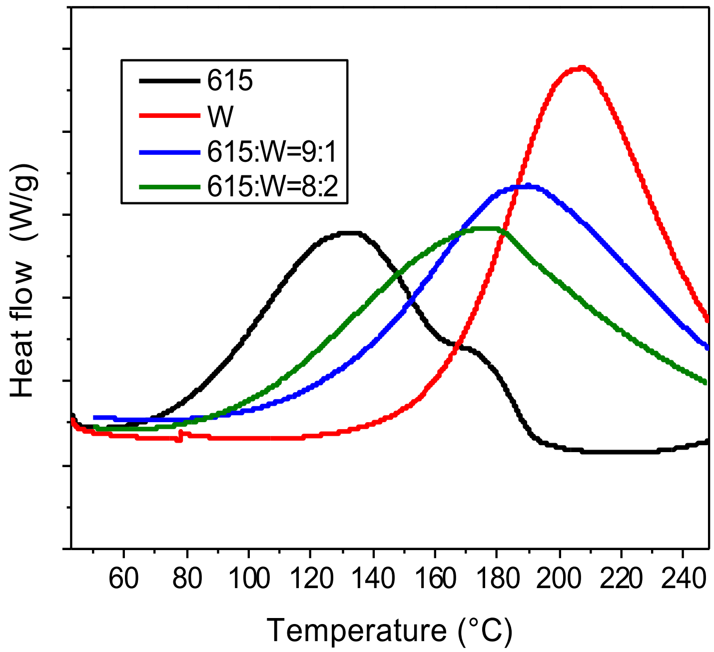
Several formulations were tested with bisphenol A and bisphenol F epoxy resins (D.E.R.™ 383 and 354 respectively) and Versamid 140 and D.E.H.™ 615 hardeners. As shown in Figure 3, the Tg's range from 67 to 78 °C. As expected, the epoxy derived from bisphenol A (D.E.R. 383) gave higher Tg's than formulations based on bisphenol F.

Figure 3: Formulation Tg



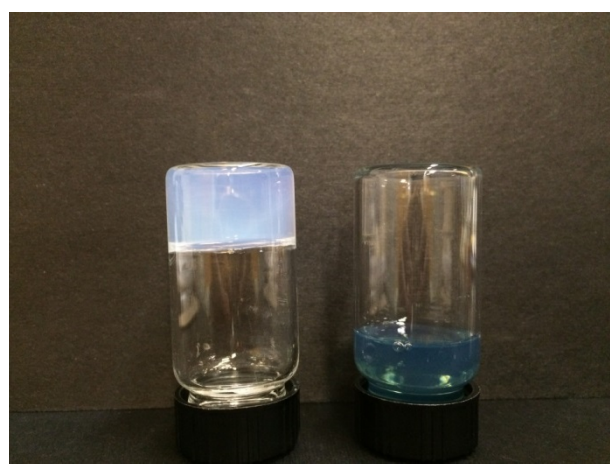
We also investigated mixtures of curing agents in an attempt to speed the cure at 100 °C. In Figure 4 several formulations with epoxy mixed with either D.E.H.615, Epicure W, and 2 mixtures are shown. It appears that only the formulation with 100% D.E.H.615 will cure at an adequate rate at 100 °C.

Figure 4: Cure kinetics with D.E.R. 383 with 4 hardeners using DSC at 10 °C/min



One problem was that the curing agents that contained relatively basic aliphatic amines (D.E.H. 615 and Versamid 140) caused the ZrP-Jeffamine M1000 to form an 'agglomerate' or gel. Two images in see Figure 5 show vials with two formulations freshly prepared and then inverted after 10 minutes. This agglomeration is faster with Versamid 140 than D.E.H. 615. Our hypothesis is that this is due to proton exchange between the Jeffamine M1000 and the aliphatic amine.

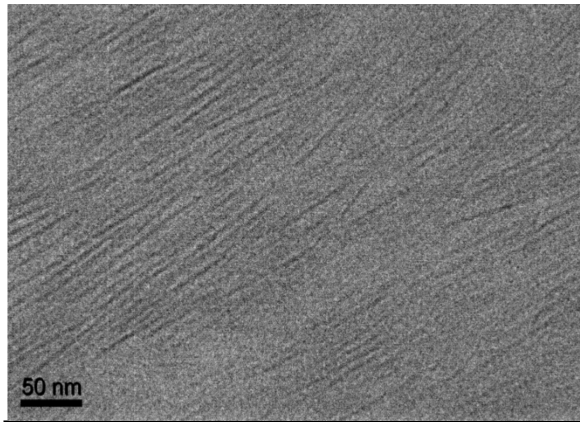
Figure 5: Agglomeration of ZrP-Jeffamine M1000 with D.E.H. 615(left) and Epicure W(right)

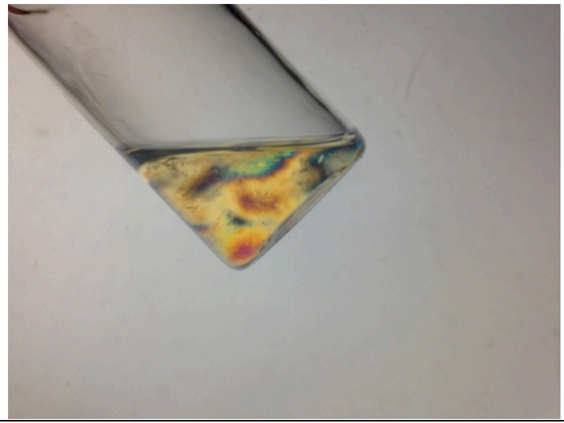


With D.E.H. 615 we managed to make coatings by quick manipulation of the formulation and using reduced percent solids in the formulation (more acetone). However, this is a potential problem that needs work to understand and fix. One option is to use a surfactant other than Jeffamine M1000, or perhaps less basic (but still reactive) amines.

Despite this difficulty, the morphology of the ZrP in the cured coating showed regular orientation, which is critical to the barrier performance of these coatings. In Figure 6, the image on the left is a transmission electron micrograph that shows regular spacing of the ZrP nanoplatelets. This regular orientation is also shown in an optical image taken of the fresh formulation between polarizers. The color patterns is characteristic of a lyotropic suspension, and further confirms that the agglomeration problem does not prevent us from obtained the desired morphology in the coatings.

Figure 6: TEM (left) and photograph in polarized light (right) of ZrP/D.E.R.383 with D.E.H. 615





Plan item #3 (Spray robot)
We are currently coating panels with a hand-help sprayer, and we are concerned about reproducibility and thickness variation. We wanted to build an automated sprayer that would improve our reproducibility. A 'spray robot' was designed, the parts were purchased and modified, and a control program was written. The cost of the parts was just under $5,000. Testing is underway, and so far the robot is working well. A video of one of the preliminary tests (using solvent only) was shown during the meeting in Freeport (July 7, 2015). We are working to optimize the spray process parameters (liquid volume, spray pressure, panel-spray head distance, movement speed). Next we will compare panels sprayed 'by hand' with the robot.

3. Description of any Problems/Challenges -

In our previous report we mentioned the possibility of two problems (first two in the list below).

1. Reactive hardeners based on aliphatic amines cause the ZrP nanofiller to agglomerate. We have worked around this problem to some extent, but we need to better understand the cause.

4. Planned Activities for the Next Quarter -

- Optimize spray robot
    - Control thickness and surface quality, reduce solvent concentration (use Design of Experiment)
    - If successful coat more panels for Shawcor (Catherine: may want adhesion test)

Appendix

Meeting notes for DTPH5614HCAP05 (Improved Coating for Pipelines)

07-July-2015 at Texas A&M in College Station, TX

Phone Attendees:

- DOT - PHMSA: Jay Prothro (was not able to attend due to a family issue)
- 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:

- Mullins gave a description of the development of the spray robot: "2015-04-02 DOT pipeline meeting MJM.pdf"
- Peng Li gave a presentation on technical progress: "DOT-Peng Li 2015-04-02.pdf"
- Catherine Lam gave a presentation related to the panel test results "TAMU-28 days from D Wong Shawcor.pdf"

Notes (items in italics are action items):

- Mike Mullins presentation
  - The spray robot was assembled with parts from Nordson and Printrbot at a cost of <$5000.
  - A control program was written.
  - Preliminary testing looks promising (a video was shown of the robot in action).
  - We need to do further testing and optimization
  - **send Nordson spray manual to Shawcor and Dow (done)*
- Peng Li presentation
  - 100C cure target with several formulations
  - ZrP aggregation
  - 2 DEH615 formulations used to coat panels sent to Shawcor
  - Surface roughness is higher with ZrP, might not be a concern for internal (not external) coatings
  - Mixed curing agents vs roughness (Dennis: there are 'levelers' that can be added
  - Eventually need to run scratch tests
  - Coatings are ~35 um

- Catherine Lam (Shawcor) presentation:
  - Cathodic disbondment at 5 temperatures (usually do 3 replicates)
  - Top row is pure epoxy coating, bottom row has ZrP (100% solids 10 mil Tg 120C underneath TAMU coating)
  - With TAMU coating, disbondment area is smaller and more consistent, about the same at higher temperatures
  - Requirement is 10 mm (but matter of pass/fail)
  - Might be a result of Tg (ours is 56C by DSC, means ~50C)
  - Dennis: need more work, but still encouraging
  - Hot water immersion test 28 days (with TAMU coating adhesion rating improved from 2 to 1 – CSA Z245.20 cross 12.14 test for fusion bonded epoxy), key is water diffusion kinetics (CD is more complicated), rating of 5 is the whole rectangle comes off in one piece
  - Lingyun, there is a phenolic coating (1-2 mil) for internal coatings that gets a powder top-coat, also surface roughness would not be an issue

- Note that HWI test is above Tg
- May want to measure the water absorbtion during HWI
- Shawcor: need to coat entire panel (4 by 12”, might be able to cut in 2)

Plans for next quarter

- Optimize spray robot
  - Control thickness and surface quality, reduce solvent concentration (use Design of Experiment)
  - If successful coat more panels for Shawcor (Catherine: may want adhesion test)
- Industry desires: Tg 110-120C, get rid of solvent (OK for higher temp cure), reactive diluent (maybe benzyl alcohol but prefer none), BYK additives

ShawCor
Energy Services • Global Solutions

June 30, 2015

Dr. Hung-Jue Sue
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RE: 3rd quarter industrial support for DOT pipeline project DTPH5614HCAP05

Dear Dr. Sue:

Our 3rd quarter support for the quarter for staff time, expenses, and materials is $4749.73. A breakdown of this total is shown below.

Project Activity	**Contributed Cost in $**
Staff time for coating formulation, testing, evaluation, meetings	4650
Materials, sample preparation, consulting	99.73
Travel expenses	
Total	4749.73

Sincerely,

Dennis Wong, PhD, P Eng
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DATE: 7/6/2015

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RE: 3rd quarter industrial support for DOT pipeline project DTPH5614HCAP05

Dear Dr. Sue:

Our 3rd quarter support for the quarter for staff time, expenses, and materials is $798.11. A breakdown of this total is shown below.

Project Activity	**Contributed Cost in $**
Staff time for coating formulation, testing, evaluation, meetings	248.50
Laboratory overhead and admin. services expense	549.61
Materials, sample preparation, consulting	0.00
Travel expenses	0.00
Total	798.11

Sincerely,

Lingyun He

PERSONAL AND CONFIDENTIAL