

Final Project Report

| | | |
|---|---|--|
| Project Title: EXTERNAL PIPELINE COATING INTEGRITY- One Year Extension | | |
| DOT PHMSA Advances Coatings R&D Contract # DTPH56-06-T-000022 | | |
| | Principal Investigator | Co-Investigator |
| Name | Prof. Hung-Jue Sue, PhD | Benjamin T. A. Chang, PhD, PE |
| Affiliation | Texas A/M University Department of Mechanical Eng. College Station, TX 77843-3123 | PolyLab LLC 10400 Westoffice Dr. Ste 107 Houston, TX 77042 |
| Telephone | 979 845 5024 | (713) 783-7659 |
| Fax | 979 862 3989 | (713) 783-9191 |
| Email | Hjsue@tamu.edu | Benjamin.Chang@PolyLabLLC.com |

EXECUTIVE SUMMARY

We have made significant achievements in our research program. The theme of this year research focuses on the high temperature external pipeline coating integrity study. The temperature range is limited to 60-110 °C. The high temperature mainline pipe coating materials are a 3 layer polypropylene and high T_g fusion bonded epoxy (FBE). We have made the following accomplishments:

- (1) We have developed a new “Caliper Free Film Bending” method to evaluate coating material stability after aging under dry and wet conditions at high temperatures. This test method uses only a digital caliper and is simple, inexpensive and effective. This test method can generate consistent test results to evaluate stability of coating material under thermo-oxidative and hygrothermal degradation environments.
- (2) We have developed a new adhesion test method to evaluate FBE-steel interfacial adhesion degradation after aging at high temperatures under dry and wet conditions. This test method –“Notched Coating Adhesion” requires a generation of a notch on the FBE film with a precrack. Then, the precracked FBE coated steel coupons are bent in a fixed radii mandrel bending machine. This machine is commonly used by FBE coating manufacturers and FBE applicators to measure FBE flexibility. This test method can quantify FBE-steel interfacial adhesion from initial adhesion to degraded adhesion values. However, the test method requires a sophisticated skill and a large number of samples to reduce data scattering.
- (3) We have done the evaluation of FBE adhesion durability by a “wet disbondment” test. This test method uses a pocket knife and is very simple. However, our test results show that the knife test can only detect poorly adhered coating with the adhesion strength less than 200-300 psi, which is the minimum requirement for the coating-steel interfacial adhesion. The wet disbondment for the FBE immersed in 95 and 110 °C water for 12

weeks are zero for both conditions. So, the wet disbondment test is not an effective method to assess FBE coating adhesion degradation.

- (4) We have used a high temperature cathodic disbondment (CD) test design developed by 3M and ShawCor to do the high temperature CD test for the high T_g FBE at 95 and 110 °C. The radial cathodic disbondment at 110 °C is higher than the one at 95 °C for a 28-day test time. If we conduct the test for 12 weeks, the entire FBE coating exposed to the electrolyte solution will be degraded by the hypochlorite generated at the anode even though we have changed the electrolyte solution weekly. So, we should use an isolated anode to reduce the impact of hypochlorite on the degradation of FBE coating material for the high temperature CD test.
- (5) We have confirmed that the cracking of 3LPP pipeline coatings is due to a combination of high temperature thermal degradation of PP topcoat and the presence of residual stresses in PP topcoat. When the mechanical strength of the thermo-oxidation degraded PP is lower than the residual stresses in the PP topcoat, PP topcoat will crack upon cooling.
- (6) We have published a paper at the BHR Pipeline Coating Conference at Antelope, Belgium in November this year. The paper title is “Residual Stresses in 3LPO External Pipeline Coatings – Disbondment and Cracking”. This paper is the **Keynote Address** in the conference. Our pioneer work and contribution on the analysis of residual stresses in external pipeline coatings and the impact of residual stresses on 3LPO coating disbondment have been recognized by the international pipeline coating community.
- (7) We have demonstrated the usefulness and unique capability of the Scratch Test to measure FBE-steel interfacial adhesive strength *via* the use of both the ASTM scratch test (D7027-05) and FEM modeling. We have also shown that the FBE coating thickness and steel substrate surface roughness can play a significant role to reduce disbondment of the FBE coating under hrgrothermal aging conditions.

We would like to request another 6 months of extension to accomplish the following tasks:

- (a) Apply the newly developed NCA test method on liquid cured high temperature coatings to explore the feasibility of this NCA test method for liquid coating systems.
- (b) Apply high temperature thermal cracking test results to extrapolate to lower temperatures and oxygen conditions.
- (C) To run control test to verify the feasibility of the use of the scratch test to measure interfacial adhesion.

1. INTRODUCTION

In the first two years of this DOT project, we have developed tools to calculate thermal residual stresses in external pipeline coatings by both analytical and finite element analysis methods. We have identified that residual stresses can play a critical role to cause coating disbondment in the three-layer polyolefin (3LPO) pipeline coatings. This finding has made positive impact to the 3LPO manufacturers, installers, and end users. The above study was based on the three-layer polyethylene (3LPE) pipeline coating system normally designed for service temperatures below 60 °C. There is a growing need to use high temperature pipeline coatings at above 60 °C. To meet market demands, FBE manufacturers recently have developed high T_g FBE for high temperature pipeline coating applications. The high T_g FBE is different from the regular FBE

with T_g at around 100 °C. High T_g FBE has higher T_g in the range of 120-150 °C and maintains high flexibility. In this research, we have studied the pipeline coatings in the temperature range of 60 - 110 °C. In this temperature range, the possible mainline pipe coating materials are a three-layer polypropylene coating system (3LPP) and high T_g fusion bonded epoxy (FBE).

A number of requirements must be met for successful application of high temperature pipeline coatings. Since the function of a protective coating is to isolate steel substrates from its corrosive environment, coating materials must maintain material integrity within their expected service life to meet the minimum property requirements as defined by the service condition. Generally speaking, the coating material degrades under a thermo-oxidative and hygrothermal environment. The high temperature pipeline coating materials must have good thermo-oxidative and hygrothermal resistance. In addition, coating materials must also maintain good adhesion to steel substrates to isolate steel from corrosive environments. The adhesion must be good enough to protect steel substrates from the corrosive environment and to remain mechanical integrity to meet service requirement. In short, coating **material stability** and **adhesion durability** to steel substrates are the two most critical coating properties to ensure high temperature oil and gas pipeline integrity. In this study, the high T_g FBE sample is 3M Scotchkote 626-140 having a T_g of 140 °C.

Pull-off adhesion conducted in accordance with ASTM D4541 has been widely used to measure the dry adhesion of liquid cured coatings. However, the pull-off adhesion test is not applicable for FBE. FBE normally has a very high initial dry adhesion (>6,000 psi) and exceeds the machine capacity of the tensile pull-off adhesion tester. For wet adhesion testing, a glue failure mode occurs very often because the epoxy adhesive glue does not adhere to damp surface well to give a successful failure mode for the adhesion test. Since the tensile pull-off adhesion test method is not successful for FBE, the knife test is often used to assess the FBE adhesion to steel. However, the knife test is not a quantitative test method and hard to give a good description of the adhesion loss quantitatively. Therefore, in this study, we have spent a good amount of effort to develop reliable adhesion test methods to assess the adhesion durability for FBE.

The purpose of the research work this year is to study the two most critical coating properties - coating material stability and adhesion durability for high temperature pipeline coatings.

2. PROJECT DELIVERABLES

- (1) Develop a quantitative wet adhesion test method to evaluate wet adhesion degradation of pipeline coatings.
- (2) Assess the wet adhesion degradation of high T_g FBE using the newly developed wet adhesion test method.
- (3) Assess the thermal stability of high T_g FBE.
- (4) Develop a high temperature cathodic disbondment test method
- (5) Develop a new test method to assess PP topcoat cracking.
- (6) Establish the correlation between PP cracking and Material Property.
- (7) Document quarterly status and progress reports and final project report and submitted in accordance with Article VI.F.2, 3, and 4 of the Basic Agreement.
- (8) Submit papers to conference presentations and publication to NACE or other pipeline conferences.

3. INDUSTRIAL PARTNERS

The following four industrial partners, representing coating suppliers and applicator were recruited to participate in this project. Their names and committed in-kind support funds for 2009 are listed as follows.

| Company Name | Representative | Business Nature | In-kind Support, \$ |
|-------------------|--------------------------|--------------------|---------------------|
| Dow Chemical | Ha Pham, Fabio Aguirre | Epoxy, PE Supplier | 33,000 |
| ShawCor | Dennis Wong, Peter Singh | Coating Applicator | 33,204 |
| 3M Powder Coating | Sam Attaguile, Russ Hess | FBE Manufacturer | 78,000 |
| NOV Tuboscope | Bill Snider | Coating Applicator | 18,343 |
| | | Total | \$162,547 |

4. ADHESION DURABILITY

The focus of this work is testing the adhesion durability for high T_g FBE to steel substrates. We have performed (1) Scratch Adhesion Test, (2) Notched Coating Adhesion (NCA) test, (3) the wet disbondment test, and (4) high temperature cathodic disbondment test. They are described in details below.

4.1 Wet-Adhesion Scratch Test

4.1.1 Background

The wet-adhesive strength is an important property for pipeline applications in which the coating system is subjected to environmental degradation, thermal degradation, and impact damage. The coating layer debonding may occur while the interfacial adhesive strength drops significantly due to various moisture and thermal conditions.

To quantitatively evaluate the *in-situ* value of wet-adhesive strength is not an easy task. A reliable and repeatable methodology is essential for this purpose. The polymer scratch test based on ASTM D7027-05, ISO 19252:2008 can be used to assess the adhesion quality of FBE coatings on metal substrates with help of finite element modeling. To measure the *in-situ* wet-adhesive strength, the immersed coating samples were scratched under controlled conditions. After experimentally locating the onset of coating delamination and the critical debonding load level, finite element modeling is adopted to obtain the corresponding interfacial adhesive strength.

As will be shown below, the proposed test method is practical and can reliably and reproducibly determine *in-situ* wet-adhesion strength in a quantitative fashion without complicated sample preparation.

With the established test methodology, the coating thickness effect on the wet-adhesive strength and their degradation is studied.

4.1.2 Test Procedure

4.1.2.1 Model Coating Systems

(a) Validation of the Test Protocol

This test is to validate the proposed test methodology. Three model coating systems were chosen for this purpose. The first coating system (System 1-1) is an epoxy (maroon) coating (DFT= 2 to 4 mils) on both smooth and roughened steel surfaces. The second coating system (System 1-2) is a 3M Scotchkote 626-140 FBE. The samples were spray coated on a flat, smooth steel panel then post-cured for 5 minutes at 480°F, followed by water quenching. The third coating system (System 1-3) is the same as the second except it was post-cured for 10 minutes, followed by air cooling. All the coating samples were prepared by NOV Tuboscope.

(b) Coating thickness effect study

This set of tests was designed to study the effect of various coating thicknesses on the degradation of interfacial wet-adhesive strength. Model coating systems with three coating thicknesses were used. The coating material Scotchkote 626-140 FBE was provided by 3M, but prepared by NOV Tuboscope. The coatings were ~4 mils, ~8 mils and ~12 mils in thicknesses for Systems 2-1, 2-2, and 2-3, respectively. All systems were spray coated on a flat smooth steel panel of 160 x 20 x 3 mm and post-cured for 10 minutes, followed by air cooling.

4.1.2.2 Coating Immersion Test Set-Up

(a) Immersion set up for the validation tests

Three custom-built water immersion set-ups were used to conduct long-term immersion at different temperatures (Figure 4.1-1). Fig. 4.1-1a is a 80 °C immersion water tank. Fig. 4.1-1b is a 95 °C water bath. Fig. 4.1-1c is a 110 °C pressure cooker. Thermal couples were installed for temperature reading and control. Foam isolation layers were used to help maintain the designated temperature in the tank. A pressure gauge was also installed for pressure reading for the 110 °C pressure cooker.

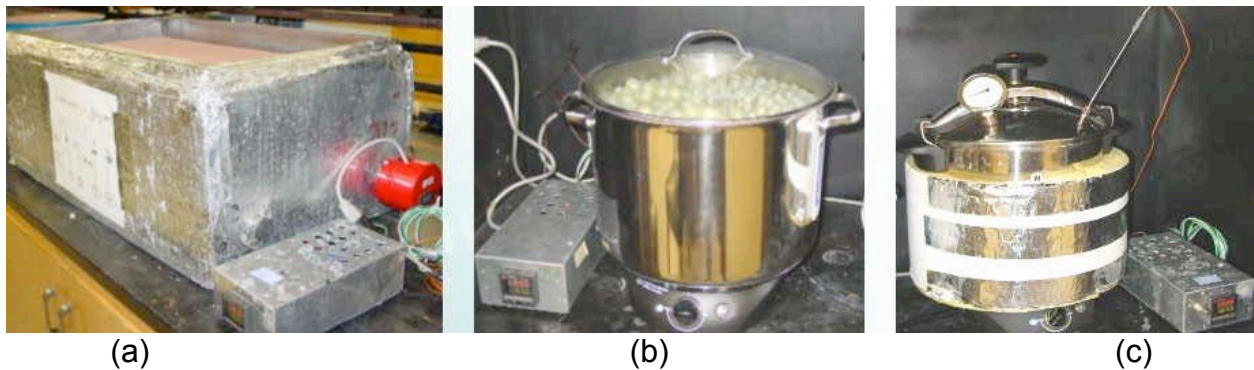


Figure 4.1-1: Custom-built Immersion Set-ups: a) 80 °C immersion tank, b) 95 °C immersion bath, and c) 110 °C pressure cooker.

(b) Immersion set up for coating thickness effect study

Here, the custom-built water immersion set-up is the same as the one shown in Figure 4.1-1c. The long-term immersion test was conducted at a temperature of 95°C. Good sealing was maintained to keep the water level.

4.1.2.3 Scratch Test

After the designated immersion time, the specimens were removed from the immersion tank, rinsed with tap water and then wiped dry. After the specimens cooled down to room temperature, the scratch test was conducted immediately. A commercially available scratch machine, SMS Scratcher IV, (Fig. 4.1-2) was utilized for the scratch tests following the ASTM D7027-05 test standard. The tangential and normal forces as well as scratch distance and instantaneous depth experienced by the stylus were recorded.

A tungsten carbide spherical tip with a diameter of 2 mm was used. The scratch test was conducted under a linearly progressive normal load from 1 to 95 N. The scratch length was set at 100 mm, and a scratch velocity of 100 mm/s was employed.

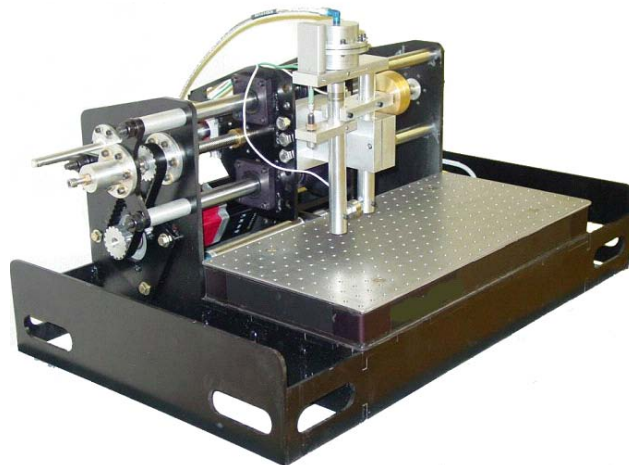


Figure 4.1-2: SMS IV scratch machine.

4.1.2.4 Onset Coating Delamination Detection

Three methods were adopted to detect the onset of coating delamination. Direct naked-eye observation, sample rusting by oxidative liquid, and a surface profile detection by Laser Confocal Scanning Microscopy (LSCM) were used to validate the findings from each other.

For the thinner coating (e.g., System 2-1 with DFT = 4 mils), the color of the coating system can be directly observed by the naked eye since the interface light reflection condition is altered by the coating layer debonding. The very first point of such a color change is defined as the onset of coating debonding. For a thicker coating, no observable color change can be observed (Figure 4.1-3). Consequently, the samples were rusted using an oxidative liquid. With one open cutting on the scratch path, the scratched sample was immersed into the DI water with 5 vol.% chlorine bleach for 6 hours. The debonded interface was exposed to the oxidative liquid and the metal surface rusts readily through capillary flow effects. The rusted portion can be easily observed to identify the onset coating delamination (Figure 4.1-4).

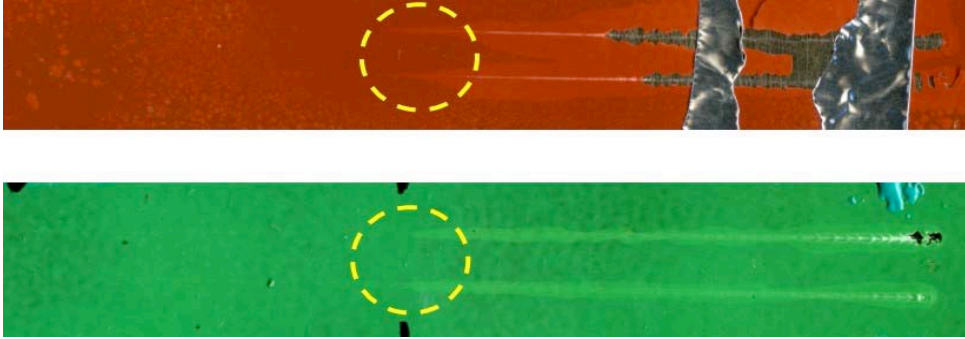


Figure 4.1-3. Color change induced by coating debonding after 1 day of water immersion: a) System 1-1 (smooth surface, 80 °C water immersion) and b) System 1-3 (smooth surface, 95 °C immersion).

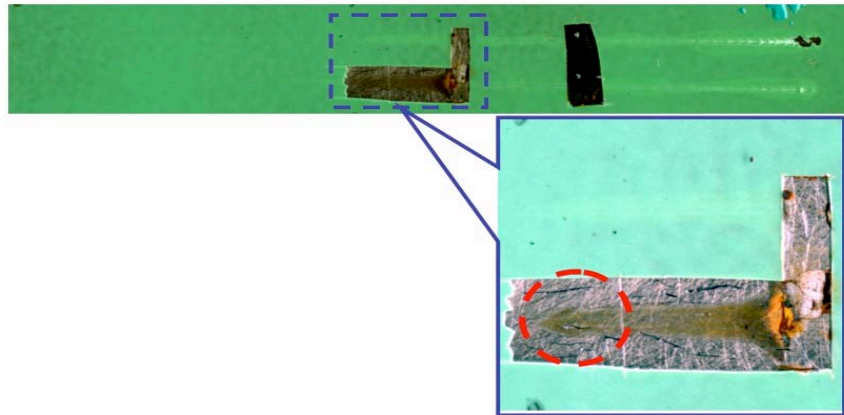


Figure 4.1-4. Determination of onset coating debonding using oxidative liquid.

If delamination occurs, the debonded coating layer will bulge and induce a subtle surface profile change, which can be nondestructively detected by LSCM observation. KEYENCE VK-9700K LSCM was used to determine the onset coating delamination.

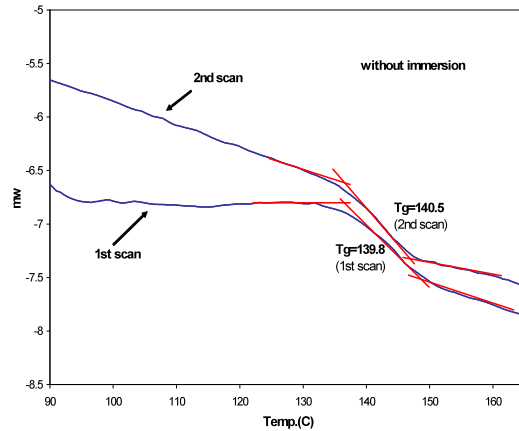
4.1.2.5 FBE Degradation Testing

Regarding the FBE material property degradation, differential scanning calorimeter (DSC; Model 821, Mettler-Toledo) experiments were conducted for the two FBE coatings with two curing conditions. Samples with and without water immersion exposure were also analyzed.

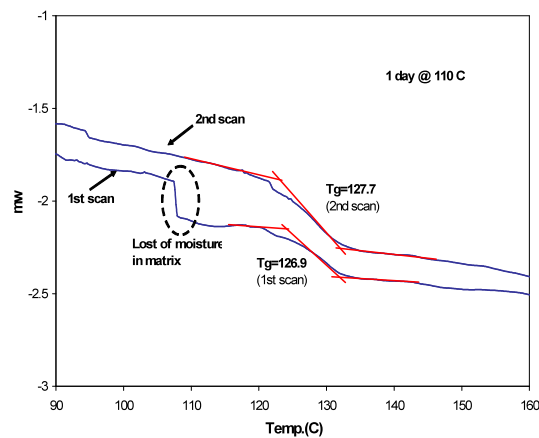
4.1.3 Results and Discussion

4.1.3.1 FBE Material Properties Degradation

The DSC curves of FBE from System 1-2 were shown in Figure 4.1-5. The T_g of the FBE material shows a significant drop from about 140°C to 126°C with only 1 day of immersion at 110°C. The DSC curves of FBE for System 1-3 show that after changing the post-cure time, the T_g of FBE exhibits a less drop from 140°C to 134°C with 1 day of immersion at 110°C and to 136°C with 1 day of immersion at 95°C, respectively.



(a)



(b)

Figure 4.1-5. DSC curves of FBE of System 1-2: a) virgin sample and b) 1 day water immersion at 110°C.

While a lower immersion temperature introduces a less T_g drop, a longer post-cure time gives FBE a better resistance against hot water degradation. Although the fundamental reason(s) for the observed T_g drop is still unknown, one can expect a very different coating scratch behavior and adhesive strength retention for these two systems after water immersion. In the case of System 1-2, the cohesive strength of the FBE coating appears to degrade quickly after water immersion. Consequently, no adhesive strength values can be obtained for System 1-2. As for System 1-3, the exposure temperature of 110°C is found to be too harsh for the FBE coating. Therefore, only the System 3 with water immersion at 95°C was chosen for the scratch tests to obtain their adhesive strength values for all tests, to be reported below.

4.1.3.2 Scratch Test

(a) Coating Thickness Effect

Scanned images of coating scratches for three systems with various coating thicknesses with an immersion time of up to two weeks at a water temperature of 95°C are shown in Figures 4.1-6 to 4.1-8. The observed locations of the onset of debonding were marked for comparison.



Figure 4.1-6: Scratch test results for coating System 2-1 (DFT = 4mils) after water immersion at 95°C. A normal load range of 1-95N was applied.

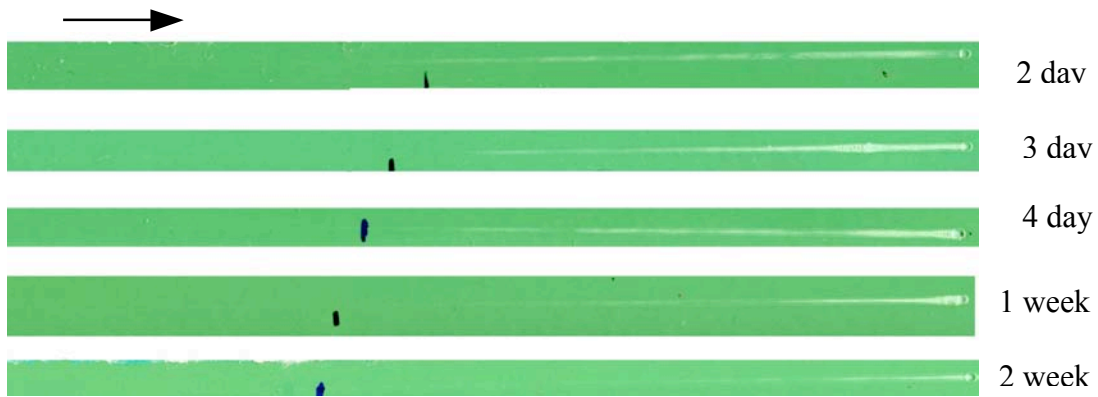


Figure 4.1-7: Scratch test results for coating System 2-2 (DFT = 8mils) after water immersion at 95°C. A normal load range of 1-95N was applied.



Figure 4.1-8: Scratch test results for coating System 2-3 (DFT = 12mils) after water immersion at 95°C. A normal load range of 1-95N was applied.

With coating delamination found on all the tested samples, the size of the delamination area and its onset location are quite different. Those differences are believed to be due to the thicker coating, which delays the water permeation and immersion degradation. At the same time, the thicker coating also requires a higher load to achieve similar stress levels to induce the debonding.

A typical image of the rusted scratch sample is shown in Figure 4.1-9. Here, the beginning point and the shape of rusted area give a good hint where the onset debonding happens. A typical LSCM three-dimensional image of the surface profile of a scratched sample is shown in Figure 4.1-10 for System 2-1 after three days of water immersion. The bulging of the scratch path can be readily observed from both the three-dimensional and the cross sectional profile of the scratch groove to identify the initial point of coating debonding.

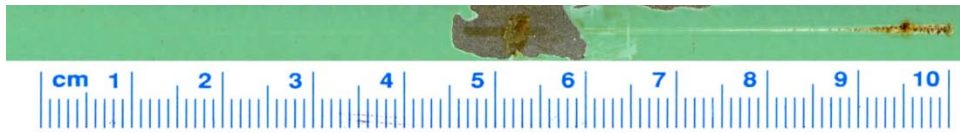


Figure 4.1-9: Onset of coating debonding detection by oxidative liquid rust for System 2-1 after three days of water immersion.

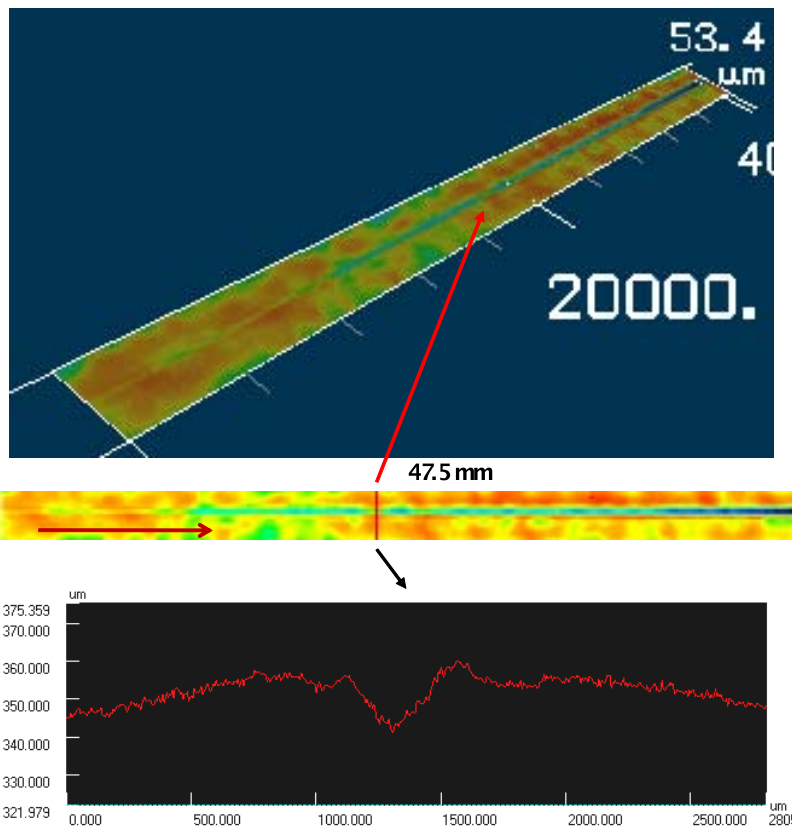


Figure 4.1-10: Onset coating debonding detection by LSCM for System 2-1 after three days of water immersion.

The values of the location of onset delamination for the three systems at different immersion time are validated by the three methods and reported in Table 4.1-1. The critical load values of debonding are also reported in Table 4.1-1. One can also find that the standard deviation (STDV) of the test results is in a reasonable range (<9%). This means that the proposed coating scratch test can generate reliable, reproducible information for wet-adhesive strength studies.

One can also find that with longer immersion time, the debonding of the coating layer occurs earlier for all coating thickness. Thus, a lower scratching load is required to induce the coating delamination with longer immersion. The degradation process is faster in the early stage of immersion and eventually levels off with long exposure time. For System 2-1 with 4 mils coating thickness after two weeks immersion, the coating layer itself becomes so weak that the cohesive damage occurs easily. Only in-layer coating damage is observed.

(b) Anchor Profile Effect on Adhesive Strength

For System 1-1 with smooth and anchor profiled steel substrate, the scanned images of coating scratch after 80°C water immersion are shown in Figure 4.1-11. As shown in Fig 4.1-11a, after three days of water immersion, the adhesive strength between the coating and the smooth substrate was weakened such that the coating delamination induced by scratch test can be detected using LSCM surface profile. Meanwhile, for the substrate with anchor profile roughening, even after 21 days of immersion, no delamination can be found. Only in-layer coating cracking is observed (Fig 4.1-11b). This illustrates the importance of substrate surface roughness on the coating adhesion performance. The proposed scratch test method can be utilized to directly evaluate how the steel surface treatment affects adhesive strength.

Table 4.1-1. Location and Load Level of Onset Debonding of FBE Coating

| Immersion Time (days) | DFT=4mils | | DFT=8mils | | DFT=12mils | |
|-----------------------|---------------|----------|---------------|----------|---------------|----------|
| | Location (mm) | Load (N) | Location (mm) | Load (N) | Location (mm) | Load (N) |
| 0 | N/A | N/A | N/A | N/A | N/A | N/A |
| 1 | 81.7±0.7 % | 77.8 | N/A | N/A | N/A | N/A |
| 2 | 51.7±5.9 % | 49.6 | 79.0±1.8 % | 75.3 | 82.5±0.9 % | 78.6 |
| 3 | 46.5±3.0 % | 44.7 | 69.5±1.0 % | 66.3 | 80.8±2.2 % | 76.9 |
| 4 | 34.7±6.0 % | 33.7 | 63.5±3.3 % | 60.7 | 79±3.6% | 75.3 |
| 7 | 25.6±8.8 % | 25.1 | 61.5±3.4 % | 58.8 | 77.5±4.6 % | 73.9 |
| 14 | N/A | N/A | 56.5±1.3 % | 54.1 | 69.5±1.0 % | 66.3 |

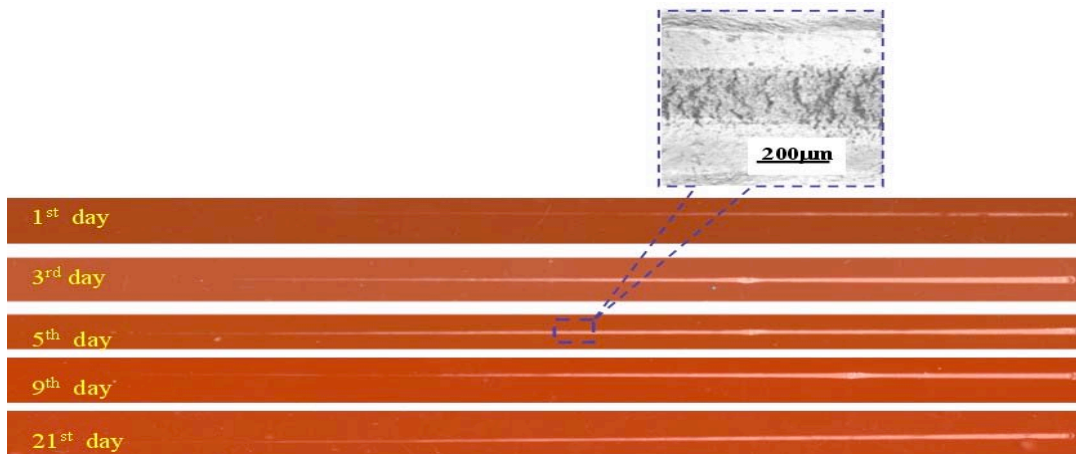


Figure 4.1-11. Surface profile effect on adhesive strength: a) smooth and b) anchor profile substrates.

4.1.4 Coating Wet-Adhesive Strength Determination *via* Finite Element Modeling

Three-dimensional FEM can be used to simulate the stress fields generated due to a progressively increasing normal load scratch process. The FEM model for the analysis is shown in Figure 4.1-12. Perfect bonding between the coating layer and substrate is assumed before the debonding happens.

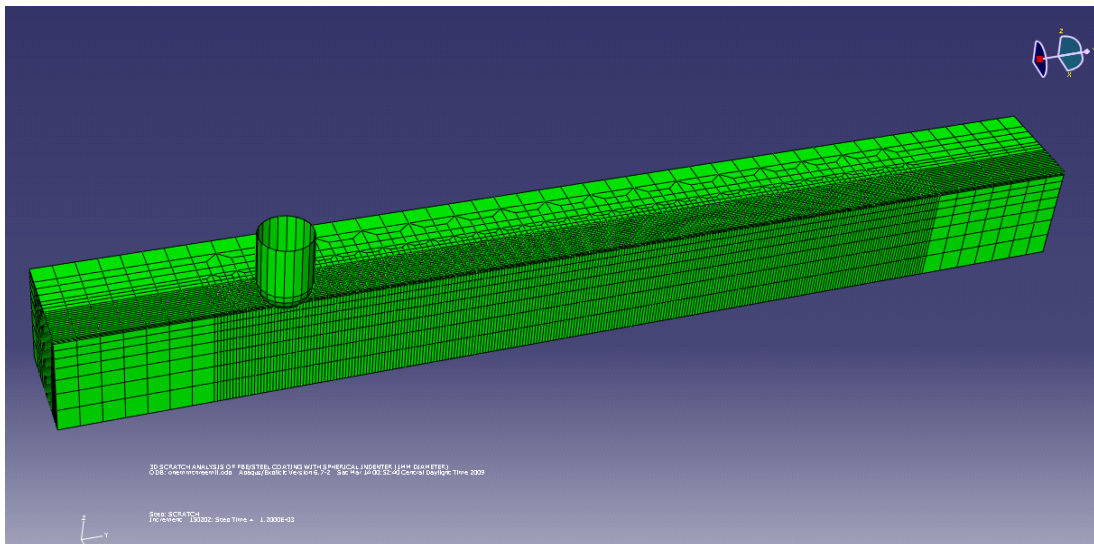


Figure 4.1-12: Finite Element Model for Coating System Scratch

The discontinuity of material properties at the interface of the coating system leads to scratch damage modes different from the bulk material. As shown in Fig. 4.1-13, the stress magnitude of the Mode I component is almost one order of magnitude higher than Mode II & Mode III stresses at the interface. Thus, Mode-I component is the dominating damage mode during the scratch process. It is also noted that the in-layer coating cohesive damage may occur if a corresponding damage criterion is satisfied. The occurrence sequence of the transverse coating crack and adhesive delamination depends on which damage stress reaches its critical level first.

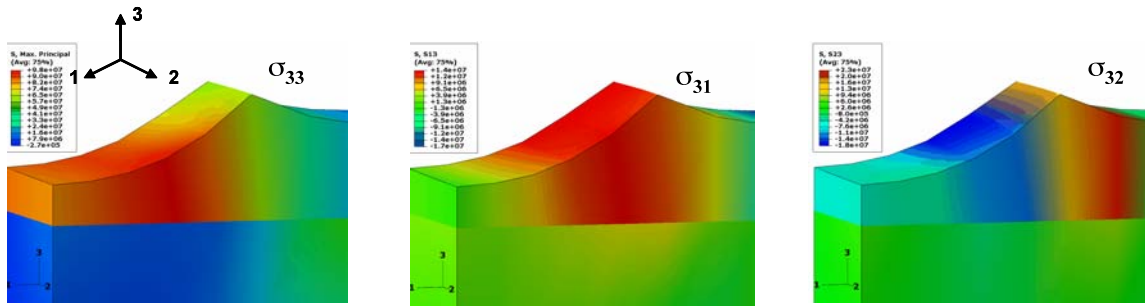


Figure 4.1-13. Stress Magnitude of the Three Possible Debonding Modes

The material properties for the FEM modeling are shown in Table 4.1-2. The occurrence of transverse crack and adhesive delamination depends on the coating ductility, adhesive strength, the ratios of E_c/E_s , σ_{yc}/σ_{ys} , and the coating thickness. Figure 4.1-14 shows the change of the debonding stress and the in-layer tensile stress as a function of the increasing normal load of scratch.

Table 4.1-2. Material Properties of a Typical Epoxy Coating System.

| | Epoxy Coating | Steel Substrate |
|-----------------------------|---------------|-----------------|
| E (GPa) | 3.8 | 200 |
| n | 0.35 | 0.3 |
| σ_y (Mpa) | 70 | 300 |
| ρ (g/cm ³) | 1.25 | 7.8 |

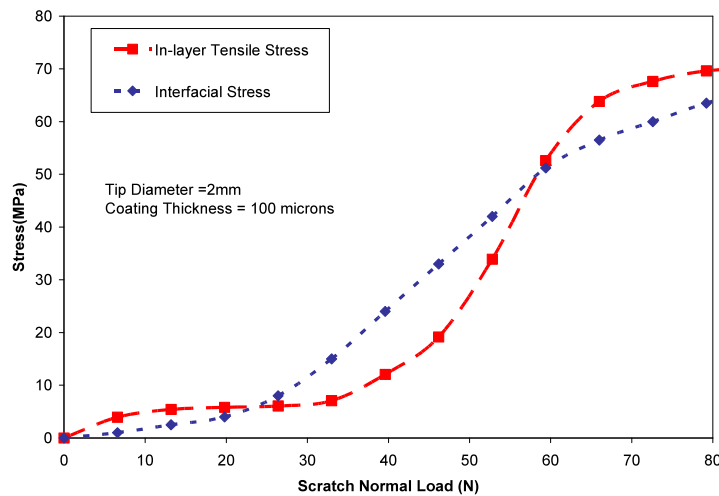


Figure 4.1-14. Interfacial Debonding Stress vs. In-layer Tensile Stress as a Function of Applied Scratch Normal Load.

With the critical load value for debonding experimentally determined in the above section, FEM modeling is utilized to assess the corresponding debonding stresses. The calculated adhesive

strengths of the three systems with three different thicknesses immersed at 95°C are shown in Table 4.1-3. The degradation of wet-adhesion strength as a function of time is quite significant. The thicker coating does slow the degradation rate in the early stage of immersion due to longer time required for water permeation. With longer immersion time, the water will eventually penetrate the coating and reaches to the interface. The ultimate degradation of interface will occur and the degraded wet-adhesive strength levels off and shows similar values for the three systems after long exposure time.

Table 4.1-3. Degradation of Wet-Adhesion Strength of Various FBE Coating Thicknesses.

| Immersion Time (days) | Adhesive Strength (MPa) DFT=4mils | Adhesive Strength (MPa) DFT=8mils | Adhesive Strength (MPa) DFT=12mils |
|-----------------------|-----------------------------------|-----------------------------------|------------------------------------|
| 0 | N/A | N/A | N/A |
| 1 | 58 | N/A | N/A |
| 2 | 41 | 47 | 50 |
| 3 | 30 | 35 | 38 |
| 4 | 18 | 21 | 23 |
| 7 | 8 | 13 | 14 |
| 14 | N/A | 10 | 11 |

4.1.5. Summary for Wet-Adhesion Scratch Test

Combining ASTM scratch test and FEM modeling, the proposed scratch test methodology for quantitatively determining in-situ wet-adhesion strength of polymer coating systems has been found to be effective. This is especially so for wet-adhesion strength determination of FBE coatings. The influences of coating thickness and steel surface anchor profile on the degradation of coating interfacial adhesive strength have been investigated. A thicker coating gives a better resistance to adhesion degradation after short water immersion time. Eventually, the wet-adhesive strength of the coatings will level off and reach a similar value after long exposure time regardless of coating thickness.

It is important to note that there are still many factors that should be considered to complete this research and to benefit the industry. These factors include, but are not limited to, (1) surface treatment effect, (2) anchor profile effect, and (3) FBE coating material property effect. If additional funding becomes available, the above research will then be carried out.

4.2 Notched Coating Adhesion (NCA) Test

4.2.1 Background

Prof. David Dillard of Virginia Polytechnic Institute and State University (VPI) has proposed the “notched coating adhesion (NCA)” test method for composites. Originally, the test method was developed for the evaluation of adhesion degradation of adhesive joints. We borrowed his test method and modified for protective coating material adhesion measurement.

4.2.2 Analytical Stress Analysis of the NCA Specimen

We assume that the coating is isotropic to act in a linear elastic fashion. A linear elastic assumption is made for the substrate.

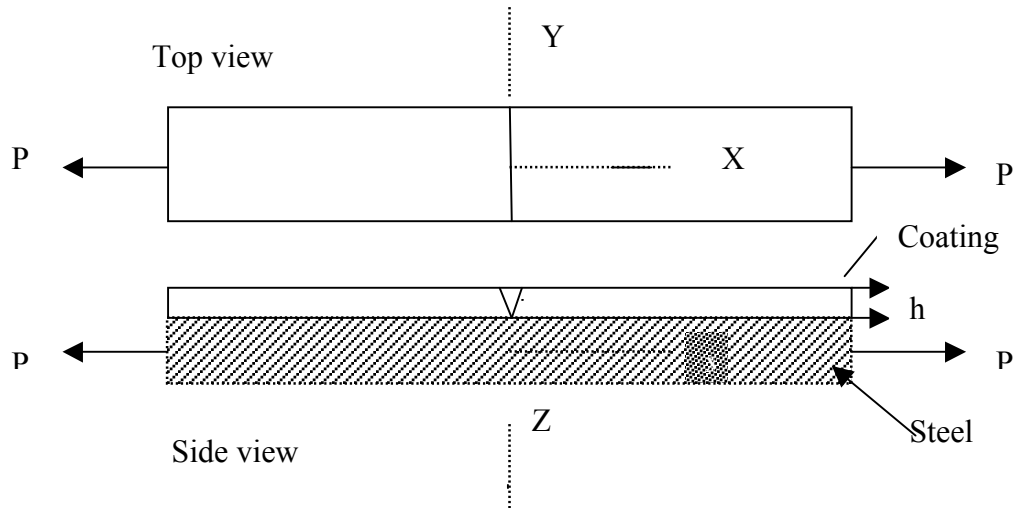


Figure 4.2-1 Notched Coating Adhesion Specimen.

For the plane stress condition, the in-plane stresses can be expressed as

$$\sigma_x = \frac{E}{1-\nu^2}(\epsilon_x + \nu\epsilon_y)$$

$$\sigma_y = \frac{E}{1-\nu^2}(\epsilon_y + \nu\epsilon_x)$$

Where E = coating tensile modulus

ν = Poisson's ratio of the coating.

An equal biaxial residual stress is present in the coating, which is related to the equal, biaxial residual strain, ϵ_0 , by:

$$\sigma_0 = \frac{E}{1-\nu} \epsilon_0$$

The residual stresses, σ_0 , result from processing the FBE coating at elevated temperature. However, the residual stresses may be relaxed upon absorption of water.

The NCA specimen is loaded axially in the x direction in order to induce debonding. The in-plane coating strains will be identical to those of the steel substrate. At a given mechanically induced axial strain, ϵ , the strains in the coating may be expressed as:

$$\epsilon_x = \epsilon_0 + \epsilon$$

$$\varepsilon_y = \varepsilon_0 - \nu_s \varepsilon$$

Where ν_s = Poisson's ratio of the steel substrate.

Combining the above equations, we obtain that

$$\sigma_x = \frac{E}{1-\nu} \varepsilon_0 + \frac{E}{1-\nu^2} (1-\nu\nu_s) \varepsilon$$

$$\sigma_y = \frac{E}{1-\nu} \varepsilon_0 + \frac{E}{1-\nu^2} (\nu - \nu_s) \varepsilon$$

The strain energy density in the coating is now given by:

$$u = \frac{\sigma_x \varepsilon_x + \sigma_y \varepsilon_y}{2}$$

$$= \frac{E}{1-\nu} [\varepsilon_0^2 + \varepsilon_0 \varepsilon (1-\nu_s)] + \frac{\varepsilon^2 (1-2\nu\nu_s + \nu_s^2)}{2(1+\nu)}$$

When the bi-axially stretched film is debonded along a straight debond front, the available strain energy release rate is:

$$G_{ss} = \frac{hE}{1-\nu} [\varepsilon_0^2 + \varepsilon_0 \varepsilon (1-\nu_s)] + \frac{\varepsilon^2 (1-2\nu\nu_s + \nu_s^2)}{2(1+\nu)}$$

The above equation may be simplified if one assumes that the Poisson's ratios of the coating and steel substrate are equal. The simplified forms assuming that the Poisson's ratios are the same are given by:

$$G_{ss} = hE \left(\frac{\varepsilon_0^2}{1-\nu} + \varepsilon_0 \varepsilon + \frac{\varepsilon^2}{2} \right)$$

The corresponding form in terms of the residual stress is:

$$G_{ss} = \frac{h}{E} [(\sigma_0^2 + \sigma_0 \varepsilon E)(1-\nu) + \frac{\varepsilon^2 E^2}{2}] \dots \dots \dots \text{Eq (4.2.1)}$$

Where G_{ss} = critical strain energy release rate, in lb/in

- h = Coating DFT in inch
- σ_0 = Residual stress in coating in psi
- E = Coating tensile modulus in psi
- ν = Poisson ratio for FBE = 0.33

4.2.3 Test Method

4.2.3.1 Specimen Preparation

The notched coating adhesion specimen consists of a thin layer of coating bonded to a substrate as illustrated in Figure 4.2-1. A FBE coated steel coupon with the dimension of 8"x1"x3/8" can be used.

4.2.3.2 Notching and Pre-cracking

After the specimen has been environmentally aged or conditioned, a notch is introduced into the coating layer to sever the coating. Firstly, use of a chisel to hit the coating surface with a hammer to generate a coating-steel interfacial precrack. The setup is shown in Figure 4.2-2. A concomitant coating debonding can also occur at the edge of the indenter and extend for a

distance to form a sharp-tipped debond between the coating and the substrate. The notching process places significant stress on the interface, usually producing sharp-tipped cracks propagating along the interface.

4.2.3.3 Crack Propagation

The specimen is loaded in bending by a fixed radii mandrel bending tester. The critical strain at which the debond starts to propagate is recorded. The debonding can be observed from the side of the specimen after each bending testing. The critical strain is defined as the strain where the initial debond begins to propagate. The primary concern when performing the NCA test is consistently determining the initial debonding stage. This determination is a source of experimental error since it depends on the reactions and discretion of the experimenter.



Figure 4.2-2 NCA Test Setup to Generate a Precrack.



Figure 4.2-3 Fixed Radii Mandrel Bending Machine.

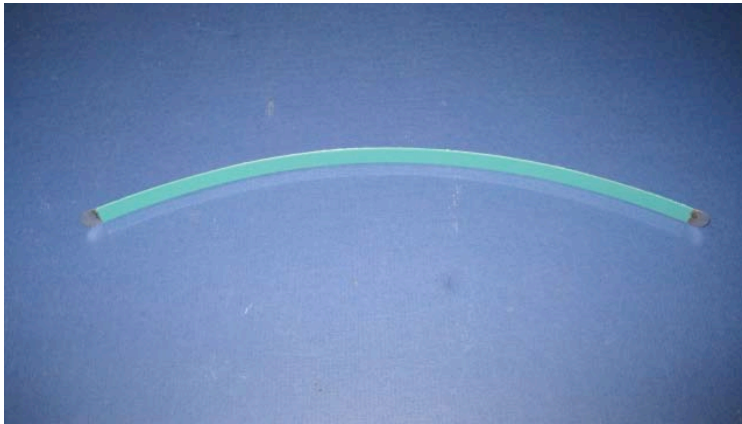


Figure 4.2-4 Residual Stress Measurement by Beam Bending Method.

4.2.4 Test Results on NCA Test Method

The strain energy release rate for the FBE coating – steel interface, G_{ss} , is described in Equation (4.2.1). In order to calculate G_{ss} , the FBE modulus and the residual stress must be known.

4.2.4.1 Young's Modulus of FBE Coating

The FBE Coating Young's Modulus, E, for Scotchkote 626-140 is measured to be 555 ksi by an Instron Tensile Machine, Model # 3369.

4.2.4.2 Poisson's Ratio of FBE

The Poisson's ratio for FBE is estimated to be 0.33.

4.2.4.3 Residual Stress Measurement

We have used the coated beam bending technique, which was developed in our DOT research work in the past two years to measure the residual stress. FBE coating of 16-10 mil DFT is sprayed onto a stainless steel 304 shim (12"x1/2"x10mil). The radius of curvature of the beam is measured. From the radius of curvature and FBE material mechanical properties (modulus and Poisson ratio), we can calculate the coefficient of thermal expansion (CTE) of the FBE sample. The residual stress for the FBE sprayed on steel coupons can, then be calculated. Mr. Bill Snider of NOV Tuboscope did a beautiful job to prepare the FBE coated SS 304 beam samples. One example is shown in Figure (4.2.4). The CTE calculated by this beam method is $3.53 \times 10^{-5} / ^\circ\text{C}$, which is very close to the CTE ($3.31 \times 10^{-5} / ^\circ\text{C}$) measured by the thermal mechanical analyzer (TMA) done by Dow Chemical. The result for FBE residual stress in the FBE coated on carbon steel coupons is shown in Table 4.2.1.

Table 4.2.1 Residual Stress in FBE coated on steel coupons at 20 °C

| Sample ID | FBE DFT, mil | Radius of Curvature, ρ(in) | Residual Stress, psi | CTE, FBE, /°C |
|------------------|---------------------|-----------------------------------|-----------------------------|-----------------------|
| 090820-A01 | 16.25 | 15.2 | 2528 | 3.62×10^{-5} |
| 090820-A02 | 16.25 | 17.4 | 2279 | 3.37×10^{-5} |
| 090820-A03 | 19.58 | 14.1 | 2490 | 3.59×10^{-5} |
| Average | 17.36 | 15.6 | 2433 | 3.53×10^{-5} |

Note: Stainless Steel 304 Shim Thickness = 10 mil, FBE Modulus = 555 ksi

Residual stress in the FBE immersed in water or aging in 110 °C air will be relaxed or increase due to dimensional swelling or shrinkage. The FBE coated steel shim is aged in 110 °C oven and RT water. We monitor the radius of curvature and calculate the residual stress. The residual stress for the FBE aged at 110 °C increases in less two days to its highest value of around 4,000 psi. The CTE is $5.0 \times 10^{-5} / ^\circ\text{C}$ for the dry FBE sample. This is the true CTE for the FBE without the effect of water absorption in ambient condition. The lower value of CTE measured on the FBE sample, which has absorbed equilibrium amount of water at RT. When we measure the CTE, the FBE is heated with a constant heating rate. When the FBE sample is heated, the FBE expands, but also loses water. Therefore, the CTE value for the RT conditioned sample is lower than the CTE for the dry sample at 110 °C. The residual stress after aging at 110 °C is approximately 4000 psi, as shown in Figure 4.2.5.

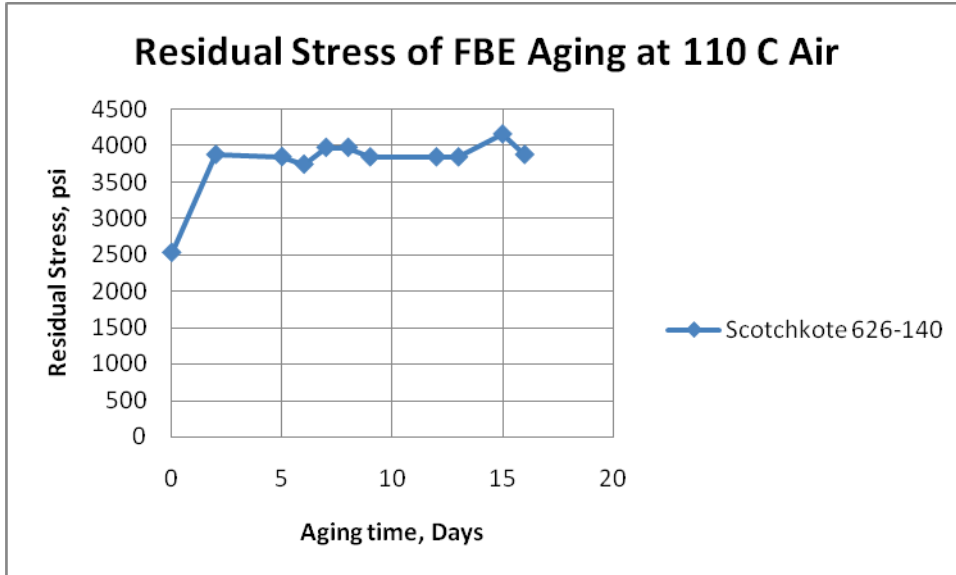


Figure 4.2-5 Residual Stress of Scotchkote 626-140 Aging at 110 °C Air.

When the FBE sample is immersed in RT water, the FBE expands to relax the residual stress. The residual stress decreases with increasing immersion time and the level-off residual stress level is approximately to be 600 psi, as shown in Figure 4.2.5. At higher water immersion temperatures at 95 and 110 °C, the stress relaxation rate should be faster. The level-off residual stress levels may be lower than the one (600 psi) at RT. Since the FBE is applied on 10 mil thick stainless steel 304 shims without surface profile, the wet interfacial adhesion is very weak and the FBE can delaminate in a very short time aging in high temperature water immersion. For practical purpose, we assume zero residual stress for the FBE immersed at 95 and 110 °C water. The 95 °C water immersion was conducted in a Blue M water bath. The 110 °C water immersion was done in an autoclave as shown in Figure 4.2-6.

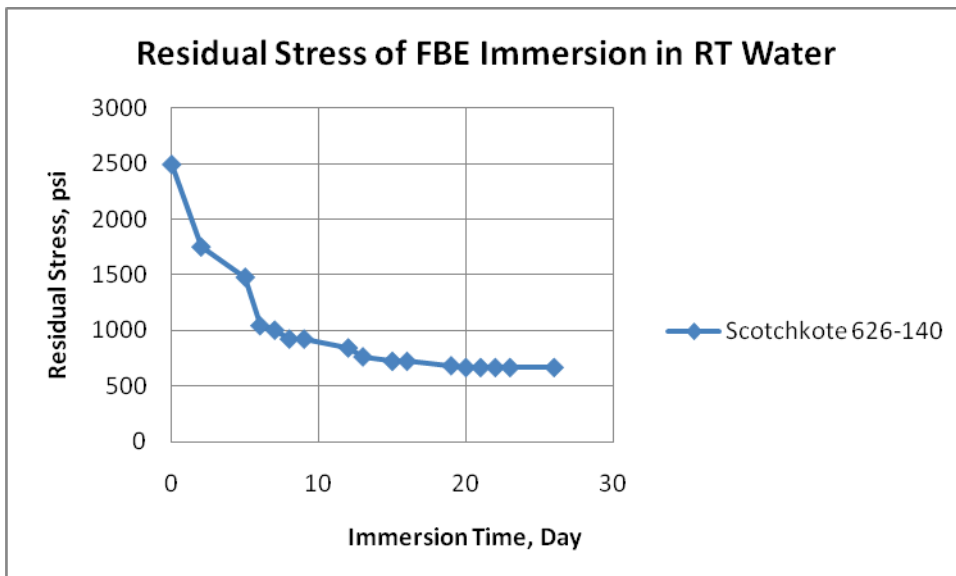


Figure 4.2.5 Residual Stress of Scotchkote 626-140 Immersed in RT Water.

4.2.4.4 FBE-Steel Interfacial Adhesion Degradation

The strain energy release rate for the FBE applied on steel coupons, G_{ss} , was measured on samples after immersion in 95 and 110 °C water and aging in 110 °C air oven. The results are shown in Figure 4.2-7 and 4.2-8. The adhesion dropped fast in an early stage of water immersion. It seems to reach a plateau and becomes stable for the 95 C water immersion. The test time is too short to see the adhesion stability for the 110 C water immersion. It is surprised to see that the adhesion for the FBE after aging in 110 °C for 160 days, the adhesion dropped to a lower value. Therefore, FBE adhesion will drop after water immersion and can also drop after high temperature aging in air. In high temperature aging in air the FBE-steel interfacial adhesion may degrade faster than immersion in water at the same temperature.



Figure 4-2.6 110 °C Water Immersion of FBE Samples in an Aluminum Autoclave.

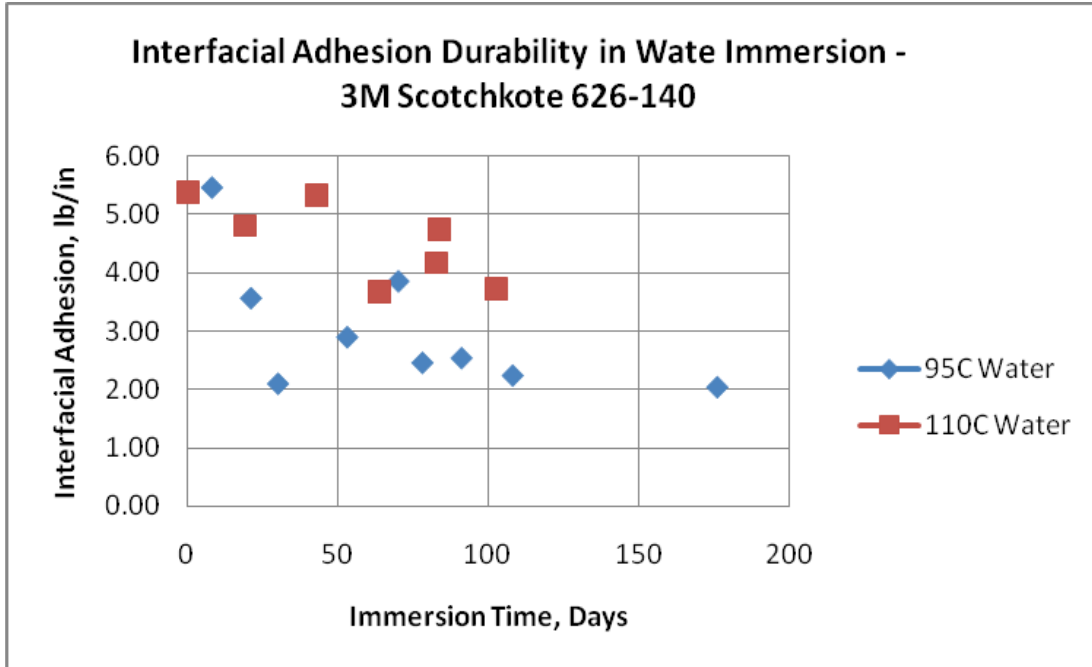


Figure 4-2-7 Adhesion degradation in 95 & 110 °C Water Immersion.
 (1 KJ/m² = 5.71 in-lb/in² = 5.71 lb/in).

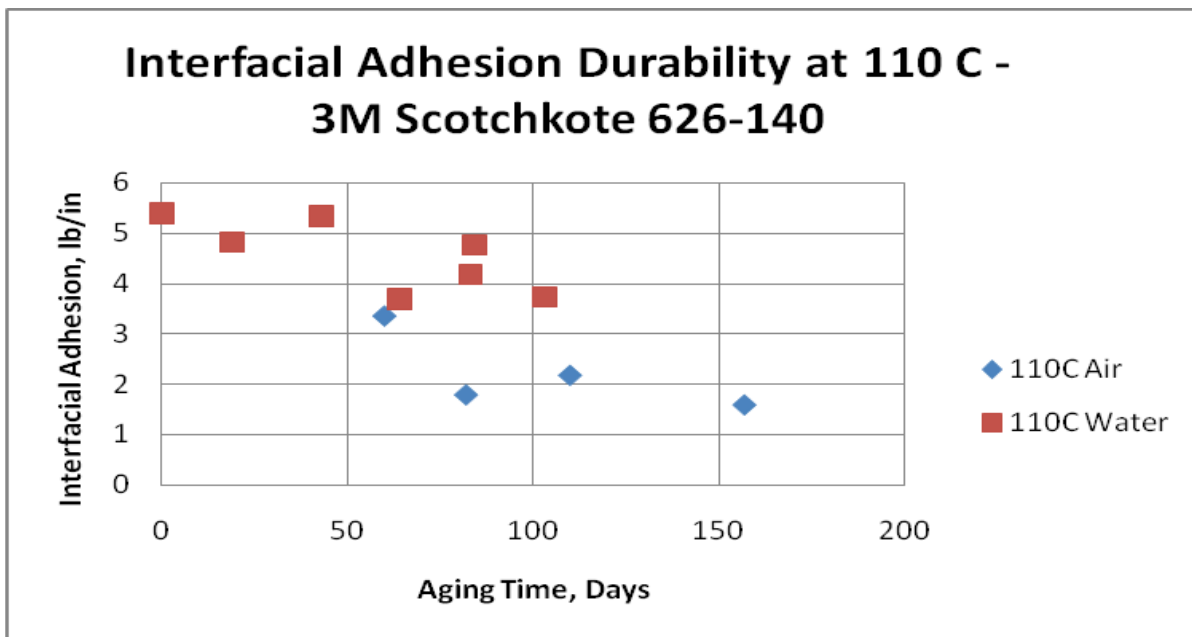


Figure 4-2-8 Adhesion degradation in 110 °C Water & Dry Air.

4.2.5 Conclusion and Discussion on NCA Adhesion Test

FBE adhesion to steel degrades after hot water immersion and it also degrades under thermo-oxidative condition. The adhesion degradation is a slow process for the FBE studied in this program. In 95 °C hot water immersion, Scotchkote 626-140 maintains a stable adhesion to steel after immersion in 95 °C water for 100 days. For the 110 °C immersion, the adhesion is high due to postcure. However, the test time is no long enough to make a fair judgment on the adhesion durability for the long term. In other words, we have not seen the adhesion reaching a plateau yet.

In the past, the coating community has seldom to study the adhesion degradation due to thermal aging in dry heat and do not think the adhesion would degrade under just dry heat. This work suggests that the dry adhesion of FBE can degrade also under high temperature dry heat aging if the temperature is high enough. The test results suggest that dry heat aging can degrade the interfacial adhesion more than in wet condition. The possible explanation is the oxidation of epoxy can degrade FBE adhesion to steel more than water does at high temperatures.

Prof. A. J. Kinloch measured strain energy release in Mode I, $G_{IC} = 0.9 \text{ KJ/m}^2 = 5.14 \text{ lb/in}$ for the precracked, tapered double cantilever steel beam with rubber toughened epoxy adhesive (Adhesion and Adhesives, Science and Technology, Chapman and Hall, Page 247.). Kinloch's result is similar to our result ($6.28 \text{ lb/in} = 1.1 \text{ KJ/m}^2$). Therefore, our adhesion test values are reasonable and the test method is considered valid.

However, the data scattering is larger than we expected. We need to do more work to refine the test technique to reduce the test data deviation.

The wet adhesion is defined as the adhesion to steel substrates when the coating system exposes to the wet service environment. For a typical service condition, the damaging factor is water degradation to the interfacial adhesion. However, for high temperature service condition, the damaging factors to the interfacial adhesion are the thermo-oxidative degradation, in addition to the hygrothermal (heat+ temperature) degradation. So far, the coating community only paid attention to the water degradation and not the thermo-oxidative damage yet. Our test results reported in this report may be the first one to report on the adhesion degradation by thermo-oxidative damage.

4.3 Wet Disbondment Test

4.3.1 Wet Adhesion Standard Test Methods

ASTM D4541 Pull-off adhesion test is the most popular coating adhesion test method in the coating industries. It has been widely used for liquid cured coatings and tested in dry condition successfully. However, it is not adequate for FBE coatings in dry or wet conditions. FBE has a very strong cohesive strength with a very high initial interfacial adhesion and glue failure is common. When FBE is immersed in water and the interfacial adhesion is degraded, the pull-off adhesion will be lower and can be measured with a pull-off adhesion tester. But the success rate is low because it is hard to glue aluminum dolly onto wet FBE coating surface. Very often, the glue failure mode occurs. Knife adhesion test is commonly used to assess FBE coating wet adhesion.

4.3.1.1 NACE TM0304 Standard

NACE TM0304 standard specifies a wet disbondment test, which is similar to cathodic disbondment test without using impressed current. A longer test time of 12 weeks is used after immersion at the hot water. In this work, 95 °C and 110 °C hot water immersion were tested. Loose coating around the holiday shall be peeled off with a pocket knife within one hour after the test specimens are removed from water. The average wet disbondment of three holidays for three test specimens shall then be calculated as a measure of the wet adhesion. The lower wet disbondment indicates better wet adhesion.

4.3.1.2 Canadian Z245.21 Standard for FBE Pipeline Coatings

Laboratory-coated test specimens shall be approximated 6.4 x 100 x 100 mm. Specimens from test rings shall be approximately 100 mm x 100 mm x pipe wall thickness.

Place the test specimen in the slow cooker, add sufficient tap water to submerge the test specimen fully, heat the water to 75 ± 3 °C for a minimum of 48 h, or 95 ± 3 °C for a minimum of 24 h, and then remove the test specimen.

While the test specimen is still warm, use the utility knife to scribe an approximately 30x15 mm rectangle through the coating to the substrate, then air cool the test specimen to 20 ± 3 °C. Within 1 h after removal from heat, insert the tip of the utility knife under the coatings at the corner of the scribed rectangle. Use a levering action to remove the coating. Continue inserting the tip of the knife and levering it under the coating until either all of the coating in the rectangle is removed or the coating demonstrates a definite resistance to the levering action.

Rate the adhesion of the coating within the rectangle as follows:

- (a) Rating 1 – coating cannot be removed cleanly;
- (b) Rating 2 – less than 50% of the coating can be removed;
- (c) Rating 3 – more than 50% of the coating can be removed; but the coating demonstrates a definite resistance to the levering action;
- (d) Rating 4 – the coating can be easily removed in strips or large chips; and
- (e) Rating 5 – the coating can be completely removed as a single piece.

4.3.1.3 NACE RP0394 “Standard Practice on application, Performance, and Quality control of Plant-applied, Fusion-Bonded Epoxy External Pipe Coating”

Laboratory-coated test specimens shall be approximately 100 mm square x 6 mm thick. Testing specimens shall be approximately 100 mm square x pipe wall thickness. For pipe smaller than 100 mm diameter, the length shall be approximately 100 mm.

Heat DI water in the container to 66 ± 3 °C. Place test specimen in the container.

After 24 hours, remove the test cell from the oven and immediately drain the water. While the sample is hot, use a utility knife to scribe a rectangle approximately 25 x 12 mm through the coating to the substrate. Air cools the sample to room temperature. The evaluation shall be performed within one hour of removal from the hot water.

The utility knife blade shall have a blade thickness no greater than 7.6 mm. If possible, insert the utility knife 3.2 mm under the coating at a corner of the scribed rectangle. Using a levering action, attempt to remove the coating. After three attempts, if the coating cannot be easily removed in pieces the size of or larger than the inserted portion of the blade, rotate to the next corner. If the coating can be removed in pieces of coating the size of or larger than the inserted blade, continue inserting the knife and levering under the coating until either all of the coating in

the rectangle is removed or the coating demonstrates a definite resistance to the levering action. Only coating removed by the levering action are considered to be adhesion loss.

Rate the adhesion of the coating within the rectangle as follows:

- (a) Rating 1 – After three attempts at each corner, the coating pieces removed are the same size as, or smaller than, the size of the inserted knife point;
- (b) Rating 2 – Rating 2 – Coating can be removed in chips that are slightly larger than the inserted knife point. Coating remained on 50% or more of the scribed area.
- (c) Rating 3 – Coating can be removed in chips larger than the inserted knife point. Coating remains on 20% or more the scribed area.
- (d) Rating 4 – The coating can be easily removed in strips or large chips considerably larger than the inserted knife point and coating remains on less than 20% of the rectangle, and ;
- (e) Rating 5 – The coating in the rectangle can be completely removed as a single piece or in a few larger chips with little effort.

4.3.2 Wet Disbondment Test Method for High T_g FBE

4.3.2.1 Equipment

The following equipment is used:

- (a) A 95 °C ± 3°C Blue-M water bath and
- (b) A 110 °C aluminium autoclave as shown in Figure 4-2.6

4.3.2.2 Test Specimen Preparation

3M has prepared the wet disbondment panels with the size of 4.5” x 4.5” x 3/8”. All six sides of the three steel panels are coated. A 6-mm (0.25-in.) holiday through the coating system in the center is drilled only on one side of each test specimen. The holiday shall be just deep enough to expose the bare steel.

4.3.2.3 Test Procedure

Three coated panels with 6 mm holiday were immersed in hot water bath at 95 °C and 110 °C for 12 weeks or longer. Enough water level shall be maintained to cover all the specimens. After immersion for 12 weeks, the specimens were removed from the hot water to be rinsed with tap water. After the specimen cools down to room temperature, loose coating around the holiday shall be peeled off with a dull putty knife or pocket knife within one hour after the test specimens are removed from the hot water. .

The radial disbondment size shall be calculated as follows;

$$RadialDisbondment = \frac{Average\ diagonal\ disbondment\ length - holiday\ size}{2}$$

The average wet disbondment of three holidays for three test specimens shall then be calculated.

All immersed test specimens shall be evaluated for the presence of blisters. Blister formation shall be measured in accordance with ASTM D 714.

4.3.5 Test Result of Wet Disbondment Test

No disbondment can be detected after 12 weeks water immersion in 95 °C water, as shown in Figure 4-3.1. Zero wet disbondment was also observed on the three panels for 103 days immersion at 110 °C, as shown in Figure 4-3.2. No blisters are observed on all panels.



Figure 4.3-1 Wet Disbondment after 12 weeks 95 °C water immersion.



Figure 4.3-2 Wet Disbondment after 103 days 110 °C water immersion.

4.3.6 Discussion on Wet Disbondment Test

Wet disbondment measurement was done with a knife, which is a simple and quick method to evaluate coating adhesion. However, this method is not a quantitative measurement. If the coating adhesion to steel is over several hundreds of psi (lb/in²), a knife cannot detect any

difference. In other words, a knife test is only a quality control tool to detect very poor coating adhesion. It cannot rank coatings for different level of adhesion above several hundreds of psi. The wet disbondment test method proposed in this program is a good quality control tool to screen the bad coatings from the good ones, although it cannot tell how good the coating adhesion is to the steel substrate. However, it is still a valuable tool for the coating industry and is very useful in discriminating well from bad coatings. The test is relatively simple to perform and do not require special or sophisticated equipment.

4.3.7 Conclusion on Wet Disbondment Test

The Scotchkote 626-140 FBE coating immersed in 95 and 110 C for 12 weeks and longer has a zero wet disbondment, which is the best performance in terms of the wet disbondment test. No blisters are observed, either. However, the knife used to make the wet disbondment measurement can only detect disbondment if the coating delaminated from the substrate at the holiday or the coating adhesion at the holiday has a very weak adhesion with less than 2-300 psi adhesion strength. The wet disbondment test method is not an effective to measure the FBE coating adhesion durability.

4.4 High Temperature Cathodic Disbondment

4.4.1 Introduction

Most of the standard cathodic disbondment test methods were developed for testing temperatures well below 100 C. At higher temperatures, there are several difficulties;

(a) Fast water evaporation

In order to reduce water evaporation, the lid over the electrolyte cell is sealed. The equilibrium oxygen solubility in the electrolyte can be maintained. Low oxygen content will reduce the cathodic disbondment to cause unjustified better performance at high temperatures.

(b) High concentration of hypochlorite

At high temperatures, the corrosion rate is high and the concentration of hypochlorite is high. The hypochlorite will dissolve the coating and cause thinning and bleaching of the coating material.

(c) Hard to keep equilibrium oxygen solubility in the electrolyte

The dissolved oxygen in the electrolyte is participating in the cathodic reaction. If it is used up, the cathodic disbondment will also be reduced. The equilibrium of dissolved oxygen in seawater is calculated to be in the following Table.

| Temperature, °C | Dissolved O ₂ , ml/L | Temperature, °C | Dissolved O ₂ , ml/L |
|-----------------|---------------------------------|-----------------|---------------------------------|
| 20 | 5.18 | 70 | 2.58 |
| 25 | 4.74 | 75 | 2.43 |
| 30 | 4.36 | 80 | 2.29 |
| 35 | 4.04 | 85 | 2.15 |
| 40 | 3.76 | 90 | 2.03 |
| 45 | 3.51 | 95 | 1.9 |
| 60 | 2.9 | 100 | 1.79 |

| | | | |
|----|------|-----|------|
| 65 | 2.73 | 105 | 1.67 |
| 70 | 2.58 | 110 | 1.56 |

For fair comparison among different test labs, the dissolved oxygen content shall be kept the same level.

(d) Metal vs. Coating Temperature

The service temperature is normally designated for the fluid product temperature in the pipe. There should a temperature gradient across the steel wall thickness and the coating surface temperature should be less than the water boiling temperature. The cathodic disbondment result should be lower if the electrolyte is boiling and bubbling during the test.

Because of the above-mentioned difficulties in the CD testing, there is no commonly agreeable standard test method to follow. This is the intention for the NACE TEG#349 x to develop a test standard and put all test parameters under the consideration. The co-investigator for this DOT project, Benjamin Chang, is the chair for this NACE TEG group (Dennis Wong is the Vice-Chair) and has been working on this program for several years.

Cathodic disbondment (CD) test is the most popular test demanded by the end users. CD test result is related to temperature and dissolved oxygen content. The higher the temperature, the lower is the oxygen content in the electrolyte and the higher the cathodic disbondment reaction rate. It is easier to run the CD test under the water boiling point of 100 °C. The purpose of this research is to compare the CD performance at 95 °C and the maximum 3LPP pipeline service temperature of 110 °C.

4.4.2 International Cathodic Disbondment Test Standards

The NFA 49-711 French Standard on three-layer external coating based on polypropylene seems to be the only standard for the higher temperature CD testing. The standard requires the use of a plastic glued to the sample by means of a chemically inert adhesive. Plastic cover with two holes that permit passage of the electrodes.

The tested metal is at the required temperature and the electrolyte should be brought to a temperature of 30 ±5C°. It is cooled by means of a chemically inert glass coil in which a coolant circulates.

4.4.3 Cathodic Disbondment Test Method

4.4.3.1 General

Both CD test apparatus design of ISO and French Standards have some weaknesses;

- (a) The electrolyte cell is sealed to prevent water evaporation. The dissolved oxygen content is getting lower with elapse time. The cathodic disbondment measurement may be lower than expected value.
- (b) The French standard uses a coiled tubing to cool the electrolyte to 30 C. The CD measurement should be much lower than the expected value.
- (c) The reference electrodes cannot be used for high temperatures.

4.4.3.2 Test Setup

- (a) Test Specimen – 4.5” x 4.5” x 3/8” steel panel coated with FBE

- (b) A glass jar of 75 mm ID with silicone rubber gasket to attach to the steel plate with mechanical clamp.
- (c) 3%w NaCl solution
- (d) Reference Electrode – Ag/AgCl in conjunction with a salt bridge to make potential measurement.
- (e) Hot plate with a steel tray containing sand as the heating media.
- (f) A glass condenser with glass coil tubing to condense the water vapor.
- (g) A stainless steel coil tubing will be used to cool the electrolyte if the substrate temperature is over 100 C.

The CD test setup is shown in Figure 4.4-1. The original test setup is from 3M and ShawCor.



Figure 4.4-1 Cathodic Disbondment Test Setup for 95 °C and 110 °C.

4.4.3 CD Test Result

The CD test results at 95 and 110 °C for 28 days are shown in Figure 4.4-1. The CD at 110 °C (7.46 mm) is indeed higher than the one at 95 °C (4.98 mm). However, for 12 weeks CD test, the entire FBE was disbonded from the steel substrate. The total disbondment is due to hypochlorite exposure, not cathodic disbondment.

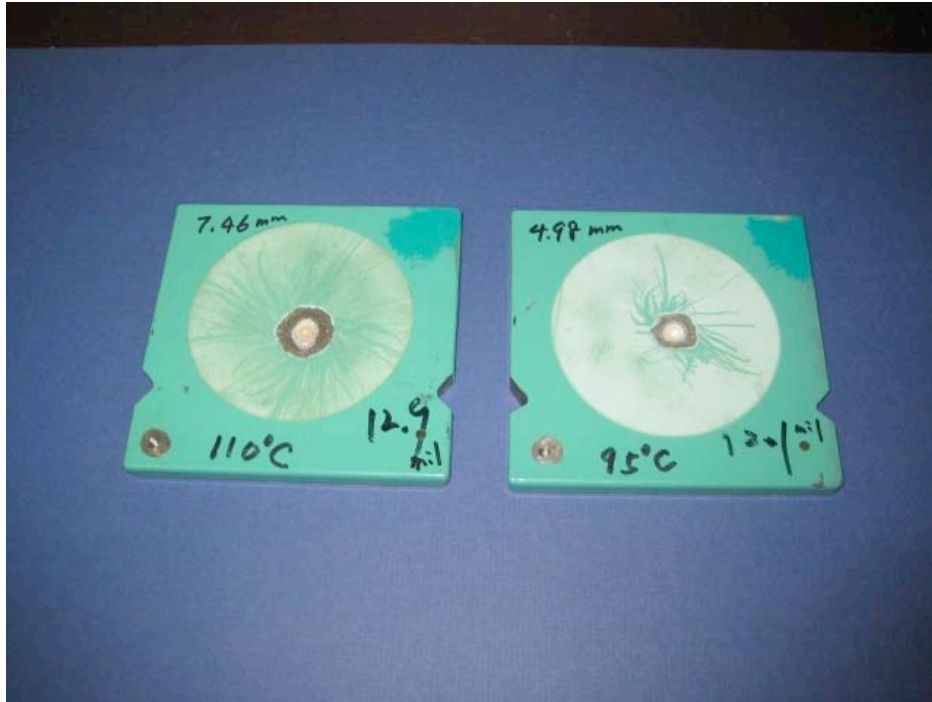


Figure 4.4-1 Cathodic Disbondment at 95 and 110 °C for 28 days.

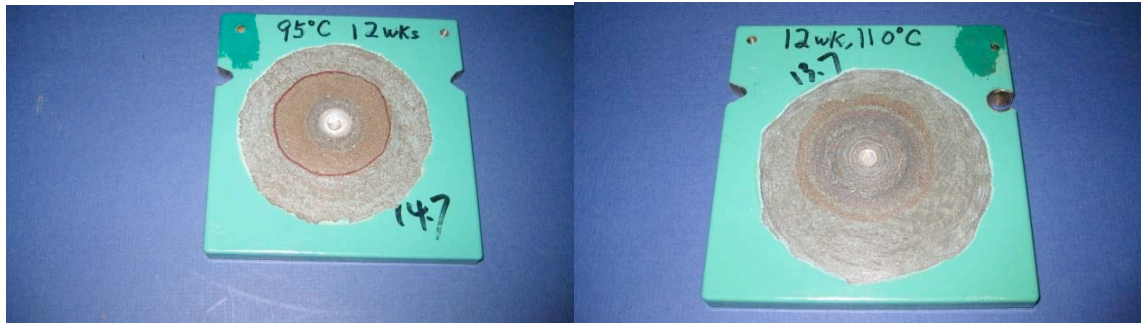


Figure 4.4-2 Cathodic Disbondment at 95 & 110 °C for 12 weeks.

4.4.4 High Temperature Cathodic Disbondment Test Conclusion

For high T_g FBE, the cathodic disbondment test shall be conducted at the maximum service temperature for 28 days. During the CD test, the test temperature shall be defined as the metal temperature. Higher temperature results in higher cathodic disbondment. The anode isolation should be installed to prevent the FBE degradation due to reaction with hypochlorite.

5. MATERIAL STABILITY OF HIGH T_g FBE

5.1 Introduction

In general, coating materials degrade under thermo-oxidative (heat + oxygen) and hygrothermal (heat + water) aging. However, coating materials must retain minimum material integrity within the expected service life. Practically speaking, the coating flexibility is a simple method to assess coating's material stability. Thermal Stability of a high T_g FBE coating has been evaluated in 110 °C hot air aging and water immersion, and 95 °C water immersion in this work.

5.2 Experimental Method

The coating material flexibility can be measured by caliper bending of free coating in accordance with ASTM B490- Standard Practice for “Micrometer Bend Test for Ductility of Electrodeposits”. The experimental method for the caliper bending of free films, as shown in Figure 5.1.

Dry air aging at 110 °C was done in an oven. Hygrothermal aging at 95 °C was done in a Blue M water bath as shown in Figure 5.2. Hygrothermal aging at 110 °C was done with an ACE Pressure Glass tube, as shown in Figure 5.3 and the tube was filled with tap water and strip film samples in a 110 °C oven.



Figure 5.1. Caliper Bending of Free Films.



Figure 5.2. Hygrothermal Aging of Coating Samples at 95 °C Water.



Figure 5.3. Hygrothermal Aging in a Pressure Glass Tube in 110 °C oven.

5.3 Experimental Results on Material Stability

The bending strain results for 95 and 110 °C water immersion are shown in Figure 5.4. The FBE flexibility drops very fast in an early stage and seems to reach a plateau afterwards in 95 °C water immersion. For the 110 °C water immersion, the FBE seems also reaching a plateau with a slightly lower retention bending strain.

The FBE material stability at 110 °C oven aging is shown in Figure 5.5. The FBE material is still under thermo-oxidative degradation in dry heat. In water, the material seems to reach a plateau. The test results reveal that the high Tg FBE will degrade under thermo-oxidative condition. While under water at the same temperature (110 C), the oxygen solubility is much lower than in the air. That is why the FBE material degrades more in dry air than in water aging at the same temperature.

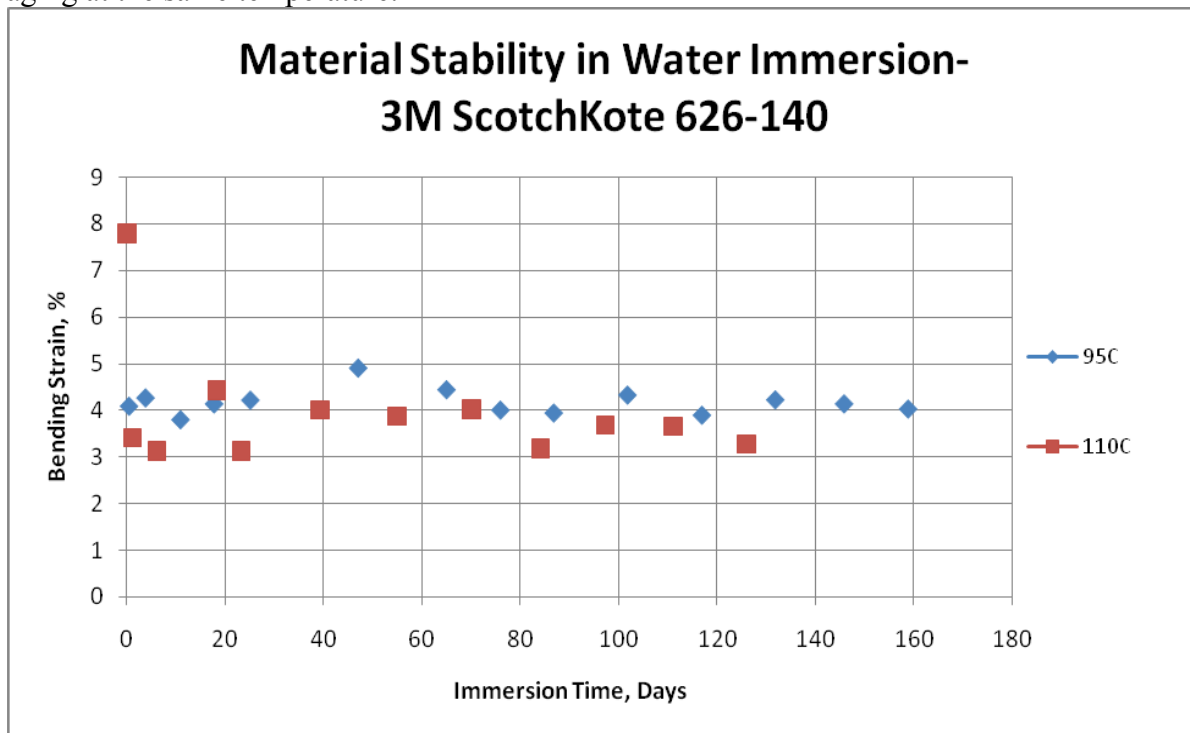


Figure 5.4 Material Stability in 95 and 110 °C Water.

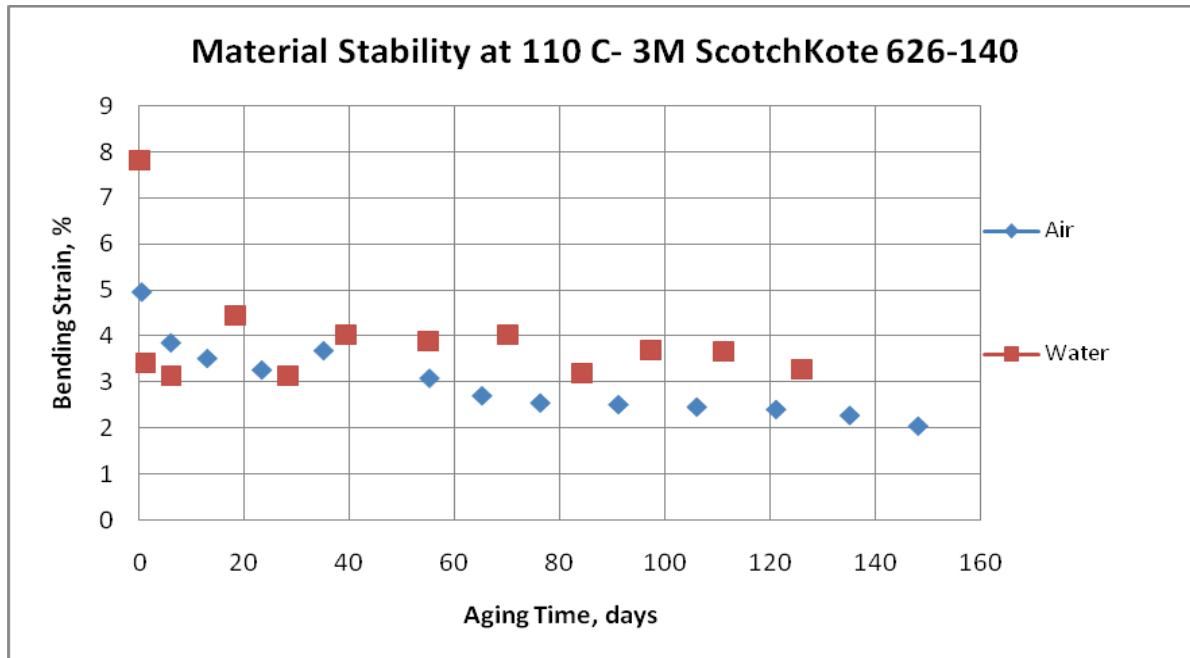


Figure 5.5 Material stability in 110 °C Hot Air and Water Aging.

5.4 Conclusion on Material Stability

Caliper bending test is a simple and effective method to evaluate FBE coating material stability under thermo-oxidative and hygrothermal aging. The Scotchkote 626-140 FBE drops its flexibility in an early stage of the aging in hot air or hot water. In 95 and 110 °C water, the material stability seems reached while in 110 °C dry air aging, the high T_g FBE is still under thermo-oxidative degradation.

6. THERMAL CRACKING OF 3LPP

6.1 Introduction

3LPP pipeline coating has been marketed as the high temperature pipeline coating with a service temperature up to 110 °C. There are many PP polymer suppliers in the world, but only two PP suppliers – Borealis and Basell are for the 3LPP pipeline coating market. Basell even claims that their PP can be used up to 140 °C. It is well-known that PP degrades under thermo-oxidative condition. The degradation rate depends on the temperature and oxygen level. To mitigate the thermal degradation, PP topcoat formulators normally add some anti-oxidant additives. For subsea application, the pipe OD temperature is low and the oxygen level is very low, 3LPP may indeed survive at high temperatures. However, for the pipeline services buried in sandy soil with high air permeability, the maximum service temperature may be greatly reduced. It has been reported that 3LPP prematurely cracked at the 110 °C service temperature in Abu Dhabi after 4 years service in the field. The PP topcoat cracking is generating a great concern for the 3LPP end users.

So far, in the coating industries, several international standards have placed attention to the PP cracking issue and have prepared standard test methods to evaluate PP cracking. The new ISO 21809-1 standard uses compression molded PP coupons the specimens and the French NFA 49-711 standard takes samples from the 3LPP pipe. The PP coupons are thermally aged in an

air-circulated oven for a period of time. Either the tensile elongation or melt flow index of the aged PP coupons is measured as indication of its thermal stability. However, these data are not sufficient to make appropriate determination on whether the PP topcoat is going to crack or not. In addition, the PP topcoat may be thermally degraded due to the extrusion process, particularly if a proper temperature control for the extruder is not maintained.

The purpose of this work is to develop an effective test method to assess the 3LPP pipeline coating cracking.

6.2 3LPP Cracking Analysis

PP has a relatively high thermal expansion coefficient than steel; their thermal residual stresses are analyzed. The residual stresses in axial, hoop and radial directions are listed in Table 3-1 and Figure 3-1. It can be readily seen that the residual stresses are quite high in PP adhesive and PP topcoat. These stresses are calculated at 20 °C. At higher temperatures, the stresses will be relaxed more. When the temperature approaches to the melting point of PP (164 °C), the residual stresses will be fully relaxed.

Table 6.1 Residual Stresses in 3LPP

| PP Topcoat | FBE | | | Adhesive | | | PP Topcoat | | |
|------------|-------------|---------------|--------------|-------------|---------------|--------------|-------------|---------------|--------------|
| DFT | hoop stress | radial stress | axial stress | hoop stress | radial stress | axial stress | hoop stress | radial stress | axial stress |
| Inch/mm | psi | psi | psi | psi | psi | Psi | psi | psi | psi |
| 0.05/1.25 | 1030 | -26.8 | 1588 | 2313 | -24.5 | 2470 | 2520 | -20.0 | 2696 |
| 0.1/2.5 | 1010 | -46.7 | 1575 | 2297 | -44.1 | 2455 | 2503 | -39.6 | 2681 |
| 0.15/3.75 | 991 | -66.1 | 1562 | 2281 | -63.2 | 2440 | 2488 | -58.8 | 2666 |
| 0.2/5 | 972 | -85.2 | 1550 | 2266 | -82.0 | 2426 | 2472 | -77.5 | 2652 |
| 0.25/6.25 | 953 | - | 1537 | 2251 | - | 2412 | 2457 | -95.9 | 2638 |
| 0.3/7.5 | 935 | - | 1525 | 2236 | - | 2398 | 2442 | -114.0 | 2624 |

ID=12 inch, Wall thickness=0.25 inch, FBE DFT = 10 mil, PE Adhesive DFT = 10 mil

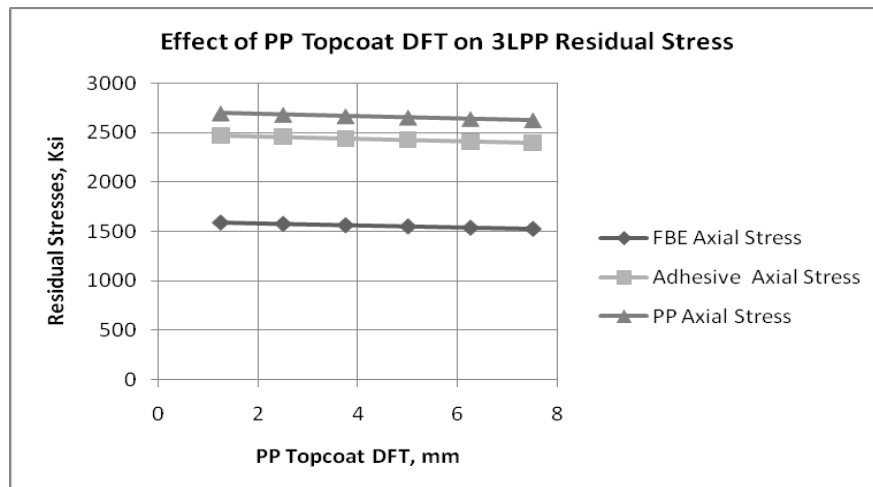


Figure 6-1 Residual Stresses in 3LPP.

6.3 3LPP Cracking Test Method and Results

It is believed that the PP topcoat cracking is due to a combination of thermal degradation of PP topcoat and the thermal residual stresses in the PP topcoat when the pipe temperature cools down during fabrication. In this work, we took the 3LPP pipe field samples sent by ShawCor and aged them in air-circulated oven at 150 °C, which is the highest accelerating test temperature we could use. The aged PP pipe samples were taken out of the oven periodically to examine visually for cracking.

A piece of 8 inches long, 8 5/8 inch OD, 9/16 inch wall thickness, 3mm TDFT plant applied 3LPP pipe samples were obtained from ShawCor and used in this test. The PP manufacturer is unknown and this pipe sample has been exposed to sunlight for some time already. This pipe sample was selected for convenience and could fit in our lab oven. Larger pipes can be used if a larger oven is available. The pipe samples were used to take into account the residual stresses present in the pipe.

The pipe sample was taken out periodically and air cooled to room temperature to check for cracking. In the beginning, we took out the sample once a week. When the 3LPP pipe sample has been thermally aged for 1,000 hours, spiral cracks started to show up. The spiral cracking, which is the same spiral wrapping during the PP topcoat application direction, can be seen in Figure 3-2. The color of the aged PP turned yellow from its original white color. When the PP topcoat was applied to the pipe, the melt PP topcoat strip was stretched and the polymer molecular chain oriented toward the wrapping direction with a higher tensile strength. On the other hand, the transverse direction is weaker. Therefore, the cracks were developed in the spiral direction first. With further oven aging, PP topcoat cracked in transverse direction is also observed, as shown in Figure 3-3. The experimental results confirm the prediction that the cracking of PP topcoat is due to thermo-oxidative degradation of the PP topcoat and the cracks were formed due to cooling, which developed residual stresses.

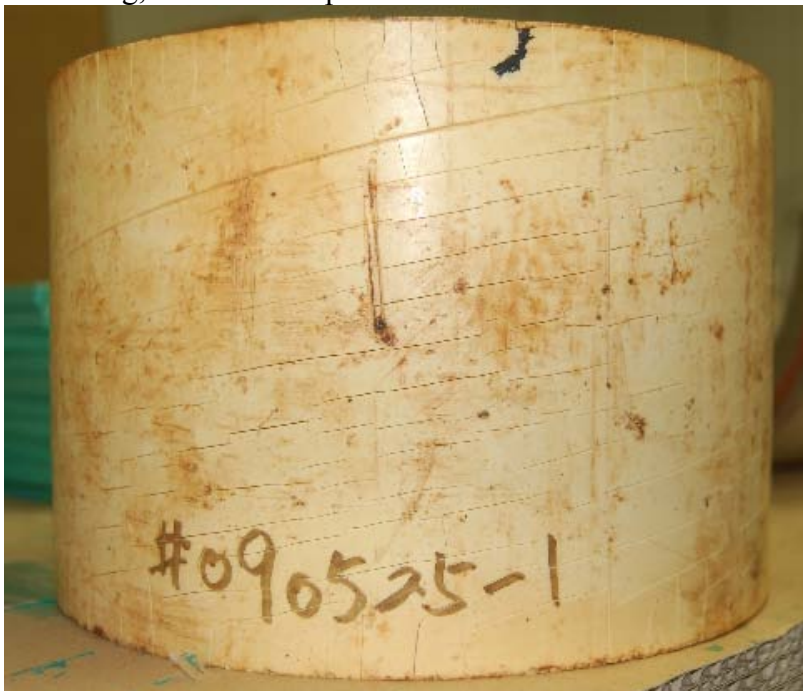


Figure 6-2 Cracking of Thermally Aged 3LPP at 150 °C Oven for 1,000 hr.

Spiral cracking appeared and the color of PP topcoat turned yellow.



Figure 6-3 Cracking of Thermally Aged 3LPP, at 150 °C for 1,000 hr + 1 wk.
In addition to spiral cracking, transverse cracking is also observed.

6.4 Discussion on 3LPP Cracking

The 3LPP material degrades under thermo-oxidation condition. The high residual stresses in the PP topcoat cause the PP topcoat cracking if the PP strength retention is below the residual stresses. In this work, we have used 150 °C thermal aging in atmospheric air with 21% oxygen content. We can use this test method to rank the candidate PP topcoat materials for their resistance to thermal degradation. However, we still cannot predict the time to crack at lower service temperatures and /or lower oxygen content. More work in 2010 is needed in order for us to make a prediction at the service temperature and oxygen content.

6.5 Conclusion on 3LPP Thermal Cracking

The test results reveal that the 3LPP cracking under high temperature service may probably be due to a combination of thermal degradation of PP topcoat and the residual stresses in the topcoat. The PP topcoat degrades under thermo-oxidative service condition. The PP is getting more brittle when it is aged. Eventually, the PP will become so brittle and its tensile strength is lowered. When the tensile strength of the degraded PP is below the residual stresses when the 3LPP cools down in thermal cycling, the PP topcoat will crack. The PP cracks will occur both in axial and hoop directions. The 3LPP cracking will be less serious if it is used for offshore application with lower seawater temperature and less oxygen concentration.