

NEW TECHNOLOGY HELPS DEVELOP COATINGS FOR HIGH-OPERATING-TEMPERATURE PIPELINES

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ABSTRACT

Pipelines that operate at high temperatures require new coating materials for protection. Development of those coating materials requires new chemistry. It also requires the development of new test methods. This paper reviews coating requirements and existing test procedures applicable to high temperature coatings. It proposes new test methods for better evaluation of the new coatings. It also provides test data and results from example candidate coatings for high operating temperature pipelines.

Key Words: fusion-bonded epoxy, FBE, pipecoating, semi-interpenetrating network, semi-ipn, high temperature, glass transition, cathodic disbondment, adhesives.

INTRODUCTION

Many pipelines operate at temperatures far above ambient. There are several reasons that include high-temperature materials coming out of the ground and materials that must maintain a high temperature. Examples include tar-sand hydrocarbons and gas with hydrates. Depending on the circumstances and environment, the pipeline coating may be:

- Single layer fusion-bonded epoxy (FBE)
- Dual layer FBE
- 3-layer polypropylene (PP)

- 3-layer PP insulation systems
- Multi-layer insulated systems

In the case of FBE systems without a polyolefin overcoat, the corrosion coating must have a glass transition temperature, T_g , above the operating temperature of the pipeline to prevent damage from pipe movement. In the case of systems with a thick polymer overcoat, the FBE is protected from damage and may be serviceable on pipelines operating above the T_g of the corrosion coating. The insulated system may be foamed or syntactic polyurethane over an FBE corrosion coating and not necessarily bonded to it. Other systems include multilayered coatings with either foamed or syntactic PP insulation layers incorporated as part of the coating system.

Whatever type of material selected, it must not only meet “normal” pipecoating requirements, but it must also provide long term performance at temperature not seen historically by underground and underwater pipeline coatings. There are many potential technologies that may address these requirements. This paper will review new FBE and PP adhesive (part of a three-layer PP system) coating technology designed for high temperature pipelines.

Potential high-temperature technologies. Due to the severity of new anticorrosion coating service temperatures, new materials must be developed to survive these more difficult environments. Common fusion bonded epoxies, customarily utilized for oil and gas pipeline protection, encounter problems because of their relatively low glass transition temperatures, which lead to issues of maintaining adhesion to steel substrates. Multifunctional epoxy resins have commonly been used to produce highly crosslinked coatings with high glass transition temperatures. FBE coatings formulated with these resins exhibit poor flexibility, poor impact resistance, and reduced adhesion to steel. However recent advances in epoxy technology have made the formulation of FBE coatings with high glass transition temperatures, good adhesion, and good mechanical properties possible.

In addition to epoxy resins, other materials may be suitable for use in high temperature pipecoating applications. One approach to making high glass transition temperature thermosetting materials has been the use of acrylonitrile-butadiene rubber toughened vinyl ester resins. Vinyl ester precursors ranging in number average molecular weight from 3600 to 3800 have been made into toughened coatings having glass transition temperatures a few degrees above 140°C .¹

Another approach to making high temperature polymeric resins for protective coatings is to graft amino groups on polyetherimides.² Coatings with glass transition temperatures ranging from 150 to 210°C were produced by this method. A 5% maximum degree of grafting was attained. The glass transition temperature showed a linearly decreasing trend with degree of grafting. Yet another approach has been the modification of bismaleimides to yield materials with glass transition temperatures of 210°C , providing good thermo-oxidative stability up to 350°C .³ These materials were prepared by reacting 4-(N-maleimidophenyl) glycidylether with bisphenols and silanediols. Polycyanurates, as products of a cyclotrimerization reaction of cyanate ester monomers, are another route to high glass transition temperatures. Studies of polyisocyanurate networks modified with polyethers have shown that blends with polyisocyanurate as the rich phase, can reach glass transition temperatures that range from 160 to 280°C .⁴

Application requirements. For greatest acceptance, new coating materials should be friendly to current application processes. That means that the coating should have gel and

cure characteristics that work with existing pipe coating mills. It also should have powder handling properties suitable for spray and dust collection systems.

Installation and handling requirements.⁵ In special circumstances, it is possible to engineer around coating limitations. For example, for a rigid coating, pipe bends are fabricated in a shop and coated in a custom application process. However, that adds difficulties to logistics, which can introduce delays and substantially increase the cost of a project.

Ideally, a high temperature stand alone pipe coating should perform as well as or better than today's commercially available pipecoating materials. For installation purposes, that means that a new coating should resist damage to impact, gouge, and abrasion. It should also have sufficient flexibility to meet field bending requirements or those for offshore installation through J-lay, S-lay, or reel barge.

In the case of three layer coatings, the corrosion-coating layer does not require the same damage resistance properties, but does require sufficient adhesion to resist delamination due to stress in the polyolefin top coat.

Performance requirements. Once the pipeline is under operation, the coating should resist damage from pipe movement and should retain adhesion and resist cathodic disbondment under the specific pipeline conditions.

In addition to stand-alone high-temperature coatings, there is also the potential for improvements in adhesive tie-layer materials used for high-temperature 3-layer PP systems.

PP adhesives designed for high-temperature 3-layer PP systems. Adhesives for three layer polypropylene or polyethylene systems are functionalized polyolefins.⁶ Common functionalities for pipeline adhesive coatings are acid and maleic anhydride (which can open into the acid form during heating or when exposed to moisture). Due to the nature of the polymerization reactions utilized for the large scale production of polyolefins and to the comparatively low adhesive production volumes, functionalization may be carried out in twin screw extruders. Unless the adhesive is made via the copolymer route, the aim is to create sites along a thermoplastic polyolefin chain to attach to available functional groups. However, the mechanisms involve chain scission, which leads to a compromise between the amount of functionality and molecular weight. Higher functional group content usually implies lower molecular weight.

Irrespective of the type of functionality, a low molecular weight adhesive will not have the thermal or mechanical properties of its initial precursor or full molecular weight resins. That means, in the case of three-layer pipeline coatings, the softening point of the linear functionalized polyolefin adhesive layer is reached before that of the full-molecular weight top coat. This creates a relatively weak link in multilayer systems, where a top coat is attached to a fusion bonded epoxy primer through these adhesives.

A further complication of the application process is that currently available adhesives can only be applied to the FBE during a very narrow time window (a few seconds usually). This is because the FBE needs to provide unreacted epoxy sites for adhesive linkage during the coating operation.

An alternative approach to functionalized polyolefin adhesives is a semi-interpenetrating network (semi-ipn (also known as Protective Network Coating (PNC)) of linear polyolefins and a crosslinkable monomeric epoxy. An advantage of the semi-ipn approach as compared to conventional functionalized olefin adhesives is that there is no significant chain scission during the functionalization step in adhesive manufacture. The reactive chemistry of a semi-ipn provides excellent binding to the FBE coating even when it is fully cured.

The melt flow index of common adhesive systems for 3-layer pipeline coatings is around 4 grams per 10 minutes (230°C, 2.16 Kg: ISO 1133). The melt flow index is the weight in grams of the polymer that flowed in ten minutes through a capillary where a given pressure (or weight) and temperature are fixed as chosen from standards. A higher melt flow index indicates lower melt viscosity and easier flow. It is difficult to tailor the melt flow index of an adhesive system due to the nature of the functionalization process. When it is desirable to fit to a set of processing parameters, a semi-ipn can be easily tailored to attain a desirable melt viscosity or melt flow index.. Semi-ipns have been made with melt indices that range from fractional, 0.8 g/10min, to 25 g/10 min. This latter melt flow range is suitable for making semi-ipn powders which can be utilized for fluidized bed dipping or spray coating, adding potentially new coating solutions to corrosion problems.

High temperature pipe coatings – What test procedures? This section has more questions than answers. That is because, as new technologies develop or old technologies are applied to new uses, the industry standards must adjust. Many of the tried-and-true test methods no longer apply.

For example, most people in the pipeline industry recognize that the glass transition temperature of a thermoset material is important. But what Tg should be used? How should the Tg be measured? With a differential scanning calorimeter, DSC, there are several protocols that affect the result, including scan rate and Tg selection method – on-set, inflection point, mid-point, or end point. Figure 1 shows examples of DSC scans. In one case, the reported result varies depending on the selection point. The other case illustrates the fact that some chemistries are not amenable to Tg measurement by the DSC method as commonly used in the pipeline industry.

DSC Test Procedure Selection Can Result in Differing Tg Values

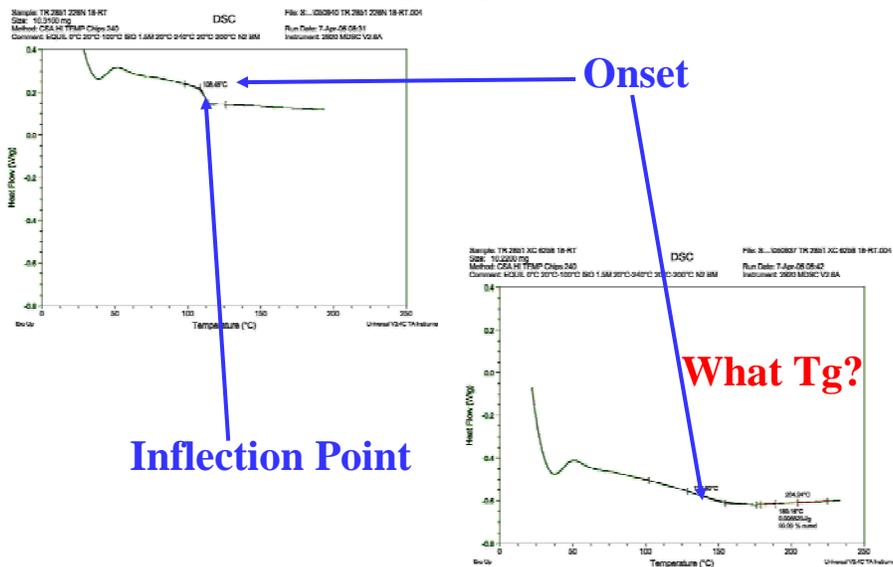


Figure 1. Within established test methods, such as DSC, which number should be used? Onset? Inflection point? End point? Some materials do not show a well defined Tg. Charts courtesy of 3M.

There are also several recognized methods for determining Tg. Dynamic mechanical analysis, DMA, is an example. Figure 2 illustrates the point with Tg values ranging from 110°C to 155°C

on the same cured FBE. Which value should be used when predicting the useful pipeline operating temperature for this coating?

Each Test Method May Give a Different Tg

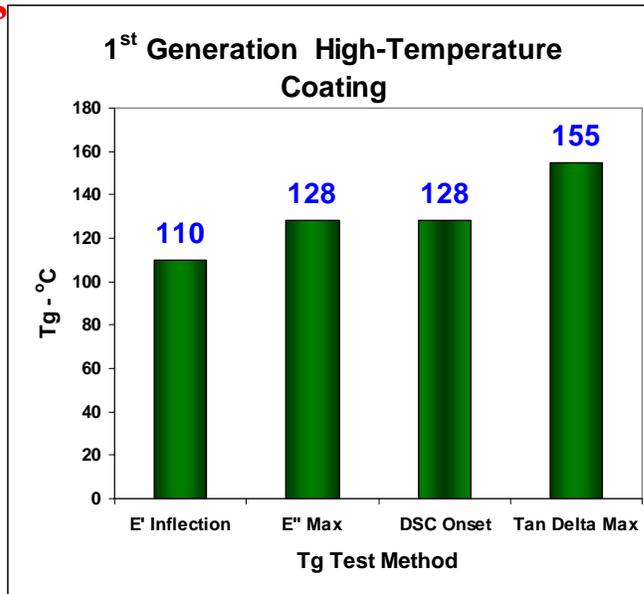


Figure 2. The chart shows the Tg of an example high-temperature FBE as measured using DMA techniques and DSC onset. Depending on the test procedure used, the reported value can be quite different. These represent a small subset of available methods and results. Charts courtesy of 3M.

One technique that can help is to go to fundamentals. A possibly oversimplified description of Tg is that it is the point where a plastic goes from being a brittle, glassy material to one that is softer and rubbery. Measuring hardness vs. temperature can illustrate the effect of going through the Tg. There are other effects as well. For example, above the Tg, a polymer picks up moisture at a higher rate and has a higher permeation rate. It is also more susceptible to damage. Figure 3 below illustrates yet another way of looking at Tg, which is to plot the surface hardness of the coating as a function of temperature. The DSC computed Tg's are shown for each curve as comparison.

Shore D Hardness vs. Temperature

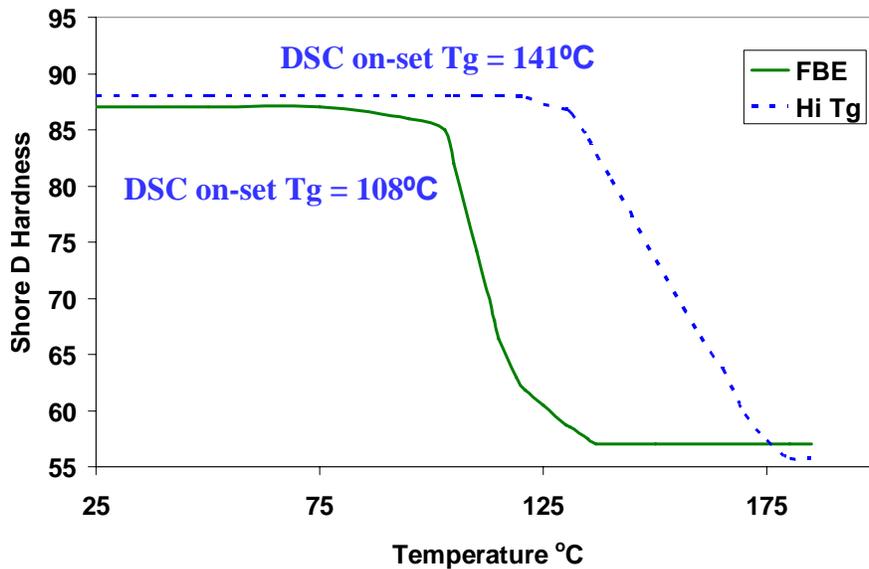


Figure 3. A physical measurement, such as hardness, can also illustrate the effect of going through the glass-transition point of a polymer. The example high-temperature FBE changed from a hard, tough coating to a relatively soft and flexible coating over a range of about 40°C. Chart courtesy of J. A. Kehr.

How important are those factors to performance as a pipeline coating? Certainly, it makes sense that a standalone coating is more susceptible to damage where pipe expansion and contraction may cause soil or rock abrasion. Is the same true when used as the corrosion coating of an insulated system or a three layer coating? One argument is that above the T_g, the FBE is more susceptible to delamination due to the stresses built up in polyethylene or polypropylene during three-layer pipecoating application. On the other hand, the FBE is protected from damage from outside forces.

A final concern about the T_g of a pipecoating is that FBE is plasticized when it absorbs water. That results in a drop in the T_g. Sourant-Moynot, et al, demonstrated a typical drop of about 20°C for many FBE pipeline coatings after exposure of a free film to 60°C deionized water for three months.⁷ Would the same effect occur with a pipeline operating at a temperature above the boiling point of water? That is, the hot-wall effect as opposed to the cold-wall effect.

Another important property of a pipeline coating is the ability to resist cathodic disbondment.⁸ There are many well understood protocols for measuring cathodic disbondment (CD) resistance of a coating. Not surprisingly, most are conducted below the boiling point of water. The reasonable question from the owner of a pipeline operating at 135°C is, "What does a 95°C test tell me about my pipeline?"

However, even the definitions are not necessarily simple when there are no clear industry standards for high-temperature CD tests. Figure 4 shows that the temperature measured depends on the location in the test cell. A reasonable argument is that the temperature at the hot plate pipe/test-plate interface most closely represents the temperature of a pipeline carrying a hot fluid. In that case, the temperature reported would be 179°C. Alternatively, by common practice, the test would be reported at the electrolyte temperature, indicating a temperature of 87°C or lower than the common 95°C. Until common industry methods and

definitions are developed, either may be reported, which requires caution on the part of the technical-paper-reading researcher.

CDT: Reported Temperature Depends on Measurement Site

Electrolyte **86.7°C**
Middle of test plate **125°C**
Interface of test plate
and hot plate **179.4°C**



Figure 4. When a data sheet reports a test temperature for a cathodic-disbondment test, what number is actually reported? In this test setup, one data sheet could report a 179°C test temperature, while another could report an 87°C temperature. It's important to know what is actually measured. Photo courtesy of 3M.

A final important property is the expected lifetime of a pipecoating. The simple test of placing a coated pipe in a 230°C oven for a few hours causes the FBE to turn brown. This illustrates that FBE is susceptible to thermal-oxidative degradation. Over time, the coating becomes brittle and eventually cracks. How important is thermal-oxidative degradation when the pipeline owner installs the coated pipe in an oxygen-depleted deep-water lay where the ocean temperature is 2°C? What if the coating is protected by a thick layer of foamed polyurethane covered with a protective outer jacket of polypropylene?

These are questions that currently do not have ready answers. To begin to search for those answers, common industry lifetime prediction tests are summarized in the section below. To begin the process of developing industry standards, NACE Task Group 336, "High Temperature Coatings for Buried and Immersed Service for Pipelines that are CP Protected" is reviewing potential test procedures.

REVIEW OF EXISTING TEST PROTOCOLS FOR PREDICTING LIFETIME OF MATERIALS

This section will focus on reviewing some key methods for characterizing lifetime predictability of polymeric materials. Various natural and accelerated testing procedures are used in the coatings industry to ensure the service life of the coated article. There is significant diversity and sometimes contradictions in the choice of testing protocols used. The test choice usually depends on the expected use and environment in which the system will be employed, and the historical confidence in a particular test. The demand to reduce product development cycles and speed the introduction of next generation products into the market highlights the need for

improved prediction tools. Service life of coated articles is dependent upon the combination of environmental attack factors, substrate preparation and coating application conditions.⁹

Proposing and establishing test methods that can be used by all in the industry must be balanced with the opportunities. Although the need and interest to work in difficult pipeline service conditions is increasing, the industry lacks clear direction and established historical data to give engineers the confidence they need to specify the long term performance of a coating solution/system. Something else that needs to be considered is literature data and hypothesized trends, obtained during these predictive examinations, to include a significant amount of detail in the procedures. This will hopefully prevent contradictory findings between testing facilities. Some authors claim that the study of the thermal degradation behavior of coatings and paints at high temperatures provides a “fingerprint” of the material that has to do not only with the characteristics of the original product, but also with its processing and the final quality of the material formed.¹⁰

Polymer Degradation Evaluations using Thermal Analysis. A typical family of methods for evaluating degradation polymers is thermal analysis. Curing reactions in thermosets proceed by addition polymerization reactions, which are temperature-dependent and determined by kinetic laws. Within this class of methods, the Kissinger method and the Flynn-Wall-Ozawa method are two that are commonly employed. However, the true mechanism of the solid-state processes cannot be handled or characterized with these models. The complexity comes in when the mechanism occurs in multiple steps that have different rates. Therefore, to better describe kinetics, iso-conversional methods can be used in conjunction with these simple thermal analysis methods.

The use of these methods allows the identification of the kinetic parameters associated with the degree of conversion at the peak of the most significant degradation processes. As a rule, the values for T_g obtained by means of different techniques are not directly comparable. Knowledge of the relationship between the T_g and the degree of conversion is required for the accurate description of the curing process. Hence, emphasizing the importance for detail when describing a solution or method (i.e., equipment used, heating rate conditions, and maximum temperatures, etc). The kinetic complexity of the thermal degradation processes, added to the oxidation reactions in oxygen atmospheres, becomes evident when polymer systems demonstrate variability of the activation energies.

The degradation of the polymer can be affected by the environment it will see while in service, both temperature and environmental. To compensate for this, authors studying these methods focus on degradation kinetic techniques in various environments (i.e., air, oxygen, and nitrogen). Thermal and thermal oxidative stability of a polymer determine the upper service temperature and environmental conditions under which the polymer can be used. Since both the initial degradation temperature and the degradation rate of the polymer are related to thermal stability, understanding the activation energy and reaction order associated with degradation becomes important.^{10, 11, 12, 13}

A study by Morancho et al., evaluated the thermal stability and thermal degradation kinetics of three common thermosetting powder coatings: polyester, epoxy and hybrid.¹⁰ The authors determined that thermal degradation processes added to the oxidation reactions where the atmosphere is an oxidizing one. This becomes evident in the variability of the activation energies obtained for the epoxy and hybrid systems. However, with the polyester system, both the activation energy and the pre-exponential factor are practically independent of the atmosphere used for thermal degradation.

At temperatures below 400°C, the rate constant of the polyester system is lower than that of the epoxy and hybrid systems. This shows that use of activation energy as the only kinetic parameter can give rise to a wrongful interpretation if the pre-exponential factor is not taken into account. With the epoxy and hybrid systems, in addition to the degradation that occurs in the nitrogen atmosphere, a second process appears at temperatures 50 or 100°C higher.¹⁰

Similar methods by Salla and others were employed to evaluate the kinetics of isothermal degradation of an epoxy thermoset powder coating in an inert atmosphere (nitrogen) and in oxidizing atmospheres (air and pure oxygen). They analyzed how the activation energy varies depending on degree of conversion and different atmospheres used. Nevertheless, the iso-conversional procedure and the changes arising in the apparent activation energy allow the processes to be tracked qualitatively.¹³

Likewise, they observed that the thermal oxidative degradation process of an epoxy powder coating is a two-stage process. The first stage of degradation is similar whether nitrogen, oxygen or air are present. The authors postulate that chain scission occurs and that there is formation of more thermally stable compounds. Without oxygen, these compounds are relatively stable at the temperatures investigated. The second stage of degradation, involving several phenomena, occurs only in the presence of oxygen or air and leads to the thermal oxidation of the organic material. These stages are very similar under non-isothermal or isothermal conditions. Through use of an integral iso-conversional procedure, they characterized the isothermal degradation processes in a nitrogen atmosphere and obtained the values for the kinetic effects, verifying that they fit well with the experimental results.¹³

Coupling Analytical Test Methods. Still others have found that coupling multiple analytical techniques might render a more meaningful understanding of thermal degradation and thermal degradation mechanisms. These coupled techniques provide structural information and enhance the understanding of the decomposition processes. The TG/DTA–GC/MS couple system is a powerful technique that is a direct measurement of weight loss, a function of temperature, the separation of products by gas chromatography coupled with a sensitive spectroscopic detector. The identification of volatile products arising from thermal decomposition can be determined by TG/DTA–GC/MS.¹¹

As discussed earlier, kinetic analysis of polymer degradation can be determined using TGA data by applying Ozawa's method. It is based on the determination of the activation energy of the decomposition process by the slope of plots of log of heating rate versus 1/T. The goal of the article authored by Parra and others is to propose the advantages of the thermal analytical techniques to better understand the degradation of powder coatings using a TG/DTA–GC/MS coupled system in the identification of the toxicological degradation products.¹¹ This study also reports kinetic parameters, for example, the activation energy of thermal decomposition for the epoxy and polyester-based powder coatings. It also suggests the application of a TG/DTA–GC/MS coupled system as a potential methodology in the investigation of the powder coatings. The system provides analysis and identification of the toxic decomposition products of powder coatings arising from their degradation.^{11, 12, 13,14, 15, 16, 17}

Other Methods. Although not included in this review, there are methods used by other industries for thermally rating the performance of polymer composites and coatings. One such method tests the flexural strength of a coated helical coil at varying elevated temperatures. The length of the exposure period and the number of coils tested per cycle will depend on the deterioration rate at each exposure temperature. The logarithms of the time in hours to reach predetermined bond strengths are plotted as a function of the reciprocal temperature (1/K) to

give an Arrhenius plot. Thermal ratings are estimated by taking the intersection of the plotted graphs with the specified time.^{18, 19}

This section reviewed methods that have been used to thermally rate materials typically used in the coatings industry. Additionally, methods that are not typical to this industry have been proposed for future consideration. Such topics as the use of coupling thermal analysis methods with other analytical techniques like TG/DTA–GC/MS as potential methodologies in the investigation of the powder coatings have been suggested. Certainly, the key properties of the system must be characterized in their present state outside of the elevated and atmospheric conditions to obtain a baseline. Then predictive models must to be confirmed with real-time and historical data to ensure accuracy.

HIGH TEMPERATURE FBE PIPELINE COATING

The properties of two high temperature FBE pipe coatings were compared to those of a standard FBE coating. The high temperature FBEs could potentially be used as either a single layer coating or as a primer in a multilayer high temperature coating system.

An ideal high temperature FBE would differ from a standard FBE only in its performance properties. It could be applied in existing coating plants using current application conditions. The high temperature FBE would also be sufficiently resistant to damage so that no special handling during transport and installation would be necessary. The damage resistant properties would be particularly important for single layer systems and less important in multilayer systems where those properties are primarily provided by the topcoat.

The high temperature FBEs were compared with the standard FBE by evaluation of application parameters (gel time, cure conditions), performance properties (resistance to cathodic disbondment, retention of adhesion in hot water) and damage resistant properties (flexibility, impact resistance). In addition some thermal and mechanical properties were compared through various analytical techniques.

The following describes test methods and experimental procedures.

Test methods. Testing was performed in accordance with the Canadian Standards Association (CSA) procedures.²⁰ In listing test methods, reference to the corresponding clause of the CSA standard is given. Any modifications made to the standard methods are noted.

Additional test methods are described below.

Thermogravimetric Analysis (TGA) was performed using a TA Instruments Model 2950 TGA. Samples were heated at 20°C per minute to 1000°C in air.

Dynamic Mechanical Analysis (DMA) was performed on thin films of cured samples using a Rheometrics Model RSA 2. Scans were made at a rate of 5°C/minute and a frequency of 1 hertz. The tensile storage modulus (E'), loss modulus (E''), and tan delta were measured.

High temperature cathodic disbondment (CD) testing was performed using the apparatus and procedure described below in the section "Evaluation of New Adhesive Materials for High Temperature 3-Layer Pipe Coatings". The thickness of the applied coating was 460 – 480 µm.

Materials and preparation of test specimens. FBE powders were used as received. Coated test specimens were prepared according to CSA Clause 6.1.2.²⁰

Application of the standard FBE powder was performed as follows. The steel panels or bars specified for the test method were blast cleaned and preheated in an oven for 1 hour at 241°C and then coated in a fluidized bed. The coated specimens were then placed in a second oven at the same temperature. After 3 minutes the specimens were removed from the second oven and immediately immersed in a room temperature water bath for 2 minutes.

The high temperature FBE was similarly applied, with the oven temperatures set at 232°C and the specimens held in the second oven for 5 minutes.

The thickness of the cured coating was 350 to 400 µm (except where noted).

Results and discussion. In order to function as a protective coating at temperatures of 120°C and above, either as a single layer coating or as a primer in a multilayer coating system, an FBE coating must be able to maintain adhesion under hot and wet conditions. Industry standard testing includes evaluation of the ability of a coating to retain adhesion to steel after immersion in hot water for an extended time period.

Since cathodic protection is applied to the pipeline, the cathodic disbondment test is important in the evaluation of pipe coatings. A coated test specimen with a holiday is subjected to conditions of cathodic protection while exposed to a sodium chloride solution at an elevated temperature. At the end of the specified test duration, the extent of the resulting disbondment of the coating around the holiday is measured.

These two tests have traditionally been used to evaluate standard pipe coatings intended for use at temperatures below 110°C. In order to evaluate the suitability of pipe coatings for use at higher temperatures, the same tests can be carried out at higher temperatures for longer times. In addition a high temperature cathodic disbondment test, capable of producing test temperatures greater than 100°C, has been developed and used to evaluate high temperature coatings.

Results of performance testing of a standard FBE coating and two high temperature FBE coatings are presented in Table 1. The results of the hot water adhesion tests carried out at 75°C and 95°C indicated that high temperature FBE coating B retained adhesion to the steel substrate somewhat better than did the standard FBE coating. In testing performed at 23°C and 65°C, the CD test results for the standard coating and the two high-temperature coatings were similar. However in CD testing at 95°C for 28 days the disbondment radius of the two high temperature FBE coatings was less than 6 mm, while that of the standard FBE coating was greater than 27 mm. Results of the high temperature CD tests showed a disbondment radius of 6.2 mm for the high temperature coating A even after 28 days at 120°C.

The application properties for the FBE powders are listed in Table 2. Compared to the standard FBE powder, the high temperature FBE powders each have significantly shorter gel times and longer cure times. The gel times of the high temperature FBEs are within the range of gel times of commercially available standard FBE coatings for pipe.

**TABLE 1
PERFORMANCE PROPERTIES**

Test	Test Method	D e s c r i p t i o n	Standard FBE	High Temperature FBE A	High Temperature FBE B
Hot water adhesion (28 days at 75°C)	Clause 12.14	Immersion in water	2 Rating		1 Rating
Hot water adhesion (90 days at 75°C)	Clause 12.14	Immersion in water	3 / 4 Rating		2 Rating
Hot water adhesion (24 hours at 95°C)	Clause 12.14	Immersion in water	1 Rating	1 Rating	
Hot water adhesion (28 days at 95°C)	Clause 12.14	Immersion in 95°C water	1 Rating ¹		1 Rating
Hot water adhesion (90 days at 95°C)	Clause 12.14	Immersion in 95°C water	2 Rating ¹		1 Rating
CD (28 days at 23°C)	Clause 12.8	1.5 V, 3% NaCl soln.	2.5 mm Radius		2.24 mm radius
CD (48 hours at 65°C)	Clause 12.8	1.5 V, 3% NaCl soln	2.3 mm Radius		
CD (24 hours at 65°C)	Clause 12.8	3.5 V, 3% NaCl soln	1.76 mm Radius	1.54 mm radius	3.75 mm radius
CD (28 days at 95°C)	Clause 12.8	1.5 V, 3% NaCl soln.	27.47 mm Radius	3.61 mm radius	5.62 mm radius
High temperature CD (14 days at 120°C)	See experimental section.			5.0 mm radius	
High temperature CD (28 days at 120°C)				6.2 mm radius	

¹Small blisters appeared along edges of test specimens.

**TABLE 2
APPLICATION PROPERTIES**

Test	Test Method	Description	Standard FBE	High Temperature FBE A	High Temperature FBE B
Gel time (seconds)	Clause 12.1	At 204°C	25 seconds	9.4 seconds	10.9 seconds
Cure conditions		Manufacturer's recommendation	110 seconds at 232°C	240 seconds at 232°C	300 seconds at 232°C

The damage resistant properties of the FBE coatings are listed in Table 3. The damage resistant properties of the high temperature FBE coatings meet the industry requirements for a single layer pipe coating. (CSA, Table 2).²⁰ Both the standard and high temperature FBE coatings exhibit acceptable impact resistance. The flexibility of the two high temperature FBE coatings is somewhat less than that of the standard FBE coating, but suitable for most pipeline installation practices.

**TABLE 3
DAMAGE RESISTANT PROPERTIES**

Test	Test Method	Description	Standard FBE	High Temperature FBE A	High Temperature FBE B
Flexibility 2.5°/PD at -30°C	Clause 12.11	Bending of coated bar over mandrel at -30°C	No cracking	No cracking	No cracking
Flexibility 3.0°/PD at -30°C	Clause 12.11	Bending of coated bar over mandrel at -30°C	No cracking	1 crack	1 crack
Impact resistance (1.5 J)	Clause 12.12	At -30°C. 6.4 mm thick plate	No holidays	No holidays	No holidays

Thermal and mechanical properties of the FBEs were measured by DSC, DMA, and TGA. The data is summarized in Table 4.

DSC was used to measure thermal properties of the powders. Tg₂ is measured after the powder is heated to 250°C and corresponds to the glass transition temperature of the cured coating. The Tg₂ values for the high temperature coatings were greater than 140°C, more than 30°C higher than the Tg₂ of the standard FBE coating.

DMA scans on cured films formed from the FBE powders were used for further thermal characterization. The DMA scans of the standard FBE and high temperature FBE A are shown in Figures 5 and 6. The peak of the tan delta cure corresponds to the glass transition temperature. As shown in Table 4 the values measured for the high temperature FBEs are 30°

to 40°C higher than that of the standard FBE. For each of the FBEs the glass transition temperature, as measured by DMA, is somewhat higher than the value obtained by DSC.

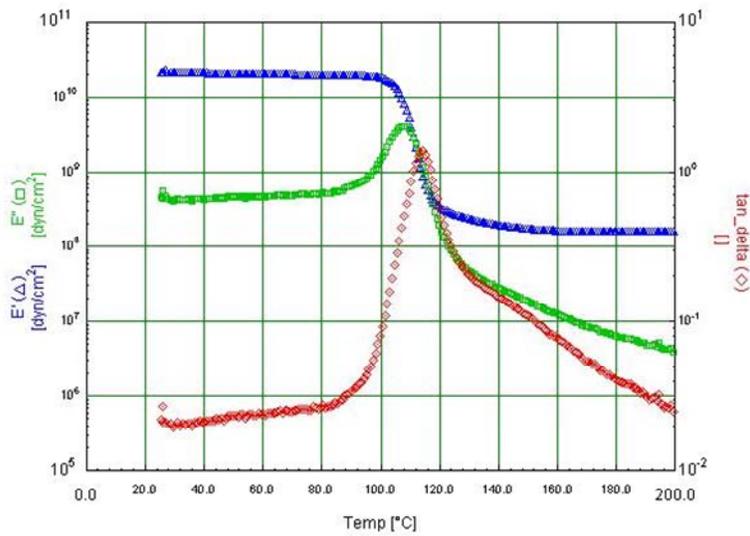


Figure 5. DMA scan of Standard FBE.

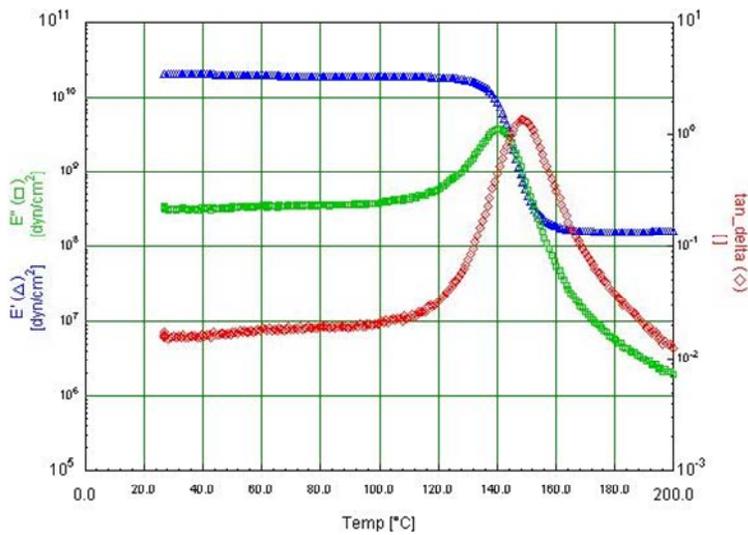


Figure 6. DMA scan of High Temperature FBE A.

The change in the storage modulus of the films with temperature is shown by the E' curve. The modulus of each of the films begins to drop at a temperature below the glass transition temperature. The onset of the modulus drop for the high temperature FBEs occurs at

approximately 130°C. Figure 7 shows a comparison of the modulus versus temperature curves for the standard FBE and high temperature FBE A.

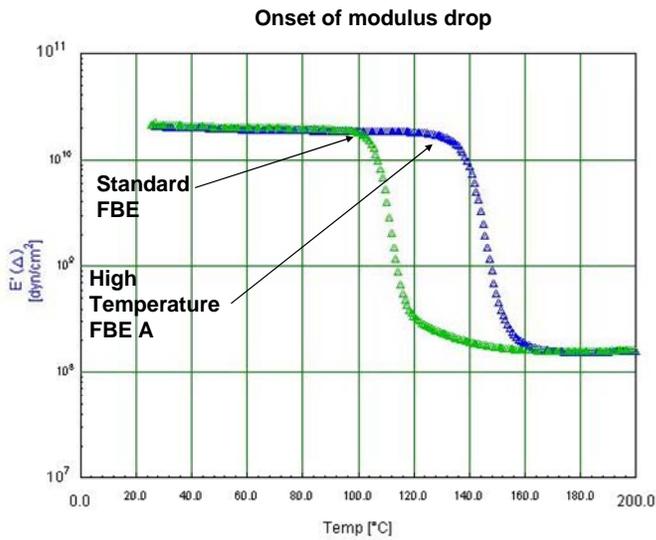


Figure 7. Comparison of the DMA storage modulus curves for Standard FBE and High Temperature FBE A.

TGA was used to measure the degradation properties of the FBEs in air. All of the FBEs began to lose weight at around 400°C. A comparison of the TGA curves of the standard FBE and high temperature FBE A is shown in Figure 8.

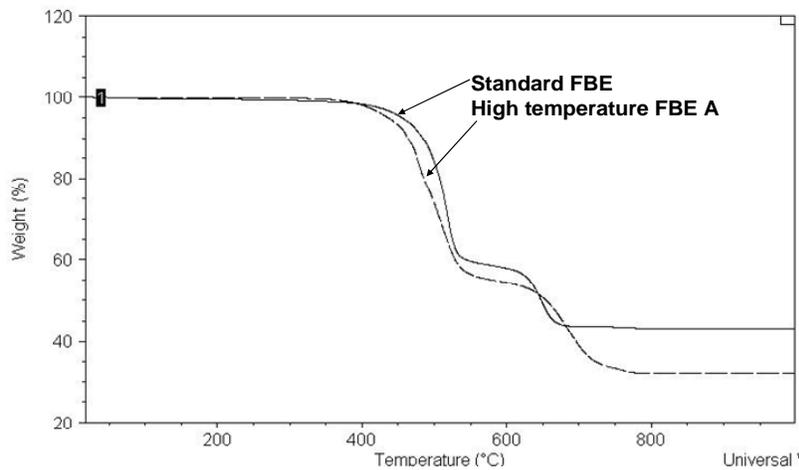


Figure 8. Comparison of the TGA curves for Standard FBE and High Temperature FBE A.

**TABLE 4
MATERIAL CHARACTERIZATION PROPERTIES**

Test	Test Method	Standard FBE	High Temperature FBE A	High Temperature FBE B
DSC	Clause 12.7 ¹ Tg1 Tg2 Delta H	63°C 105°C 59 J/g	58°C 142°C 97 J/g	51°C 143°C 116 J/g
DMA	Tg Onset of modulus drop	114°C 99°C	148°C 128°C	154°C 133°C
TGA	Onset of weight loss	415°C	405°C	405°C

¹The modified temperature cycles were used. Cycle 1: Powder samples were heated from 25°C to 75°C at a rate of 20°C per minute, then immediately cooled to 25°C. Cycle 2: heated from 25°C to 250°C at a rate of 20°C per minute, then immediately cooled to 25°C. Cycle 3: heated from 25°C to 175°C.

Glass transition temperatures are reported as the transition midpoint.

These results indicate that the new high temperature FBE pipe coatings provide acceptable cathodic disbondment resistance and adhesion retention in water as single layer coatings at temperatures where the performance of the standard FBE coating is unacceptable.

The high temperature FBE pipe coatings provided good performance at 95°C to 120°C as a single layer coating. The standard FBE pipe coating exhibited unacceptable cathodic disbondment resistance at 95°C. Evaluation of application and damage resistance properties of the high temperature FBE coatings indicated that they were similar to those of the standard FBE coating.

The poor CD test results for the standard coating at 95°C indicate that the useful operating temperature range for FBE pipe coatings as single layer coatings may be limited to temperatures somewhat below the glass transition temperature of the coating. The change in mechanical properties of the coatings at temperatures below the glass transition temperature seen in the DMA results is a further indication of the temperature limitations of the coating.

The operating temperature of the high temperature FBE coatings as single layer coatings was not defined in these experiments. Performance as part of a multilayer coating was not investigated. Further work would be necessary to fully define the suitability of the high temperature FBE coatings in either single later or multilayer pipe coating applications.

EVALUATION OF NEW ADHESIVE MATERIALS FOR HIGH TEMPERATURE 3-LAYER PIPECOATINGS

Continuing oil exploration and pumping challenges push new requirements for damage resistant coatings. Fusion bonded epoxies are now being formulated for continuous use or

service temperatures beyond 120°C. The glass transition temperature of the fusion bonded epoxy coating has significant influence on the coating's performance if exposed to a service temperature higher than the glass transition temperature.²¹ Furthermore, its corrosion protection may change due to increased susceptibility to oxygen and moisture transmission. This is especially true in three layer systems where high-melting temperature olefin layers protect a thin fusion bonded epoxy layer or primer. For cases where the fusion bonded epoxy is well adhered to the steel and well cured, softening of the adhesive layer may result from higher service temperatures. As mentioned above, adhesive layers based on functionalized linear polyolefin chains flow before their higher molecular weight top coats. Expansion and contraction of a thick rigid top coat dictates the movement of the thin layers below if they have softened. Differences in expansion or contraction between the steel pipe and a thick rigid top coat will induce coating failure whenever any of the two thin layers, primer and/or adhesive, have been compromised.

Experimental Procedure. In order to obtain a laboratory measurement of how various adhesive systems perform, 180-degree peel tests were performed using a universal tensile tester equipped with an environmental chamber. More specifically, the adhesion of linear functionalized polyolefin adhesives and semi-interpenetrating networks to fully cured fusion bonded epoxy were probed at various temperatures below and above the glass transition temperature of the fusion bonded epoxy. Additionally, cathodic disbondment measurements at high temperatures have been made to evaluate a new type of experimental fusion bonded epoxy and the semi-ipn materials.

Peel tests. Materials: Two commercially available maleic anhydride functionalized polypropylene adhesives were chosen, adhesive A, and adhesive B. The semi-ipn has polyolefins as linear molecules and crosslinkable epoxy as the thermoset. The pellet form is for wrap applications or girth weld. The powder is formulated for fluidized bed or spray coating of irregular parts or repair jobs.

Thin (40 mils) steel sheets were degreased with methyl ethyl ketone and steel grit blasted. The sheets were heated to 220°C and then dipped into a fluidized bed of fusion bond epoxy. These specimens were then placed on a hot plate and heated until the fusion bonded epoxy temperature reached 215°C. Then a pre-extruded sheet of adhesive or semi-interpenetrating network nearly 20 mils thick was rolled on top of the coated strip until it became tacky. Two halves were then joined on the hot plate and removed from the heat to be air cooled to room temperature. The specimens were conditioned at 25°C, 30% relative humidity for 24 hours prior to testing. It would have been ideal to have adhered the linear functionalized polyolefins to the fusion bonded epoxy prior to full cure, as it is done in the factory. However, it was not possible in laboratory conditions. This does not matter for the semi-ipn, which can adhere to cured fusion bonded epoxy.

The 180-degree peels were done in a Model 1122 Instron Universal Tensile Tester with a 5000 Newton load cell. The temperature in the environmental chamber, which was mounted directly on the tensile tester, can be varied from -50°C to 200°C. The rate of testing or cross head speed was 25.4 centimeters per minute. The specimen dimensions were 25 mm in width by 150 mm in length. A minimum of three trials per condition were performed.

Cathodic disbondment test. Materials. A new experimental high temperature fusion bonded epoxy was utilized. The semi-ipn, described in the previous section, was made into 12 cm wide sheets (0.75 mm thick) using a ¾ inch Brabender (Hackensack, NJ) single screw extruder, a coat-hanger sheet die and a Brabender 2 roll take off system. The roll temperature

on the take off system was 80°C. The temperature profile in the single screw extruder was: 200, 205, 210, 215°C. The pressure monitored at the tip of the extruder was 630 +/- 10 psi.

Cold-rolled steel test panels were degreased with methyl-ethyl ketone and blasted with steel grit. The panels were 6 mm thick and 10 cm per side. They were then heated to 230°C and coated using a fluidized bed with the experimental fusion bonded epoxy powder. The panels were post cured for 2 minutes at 220°C.

The final coating thickness was 200 microns for the fusion bonded epoxy coatings that were subsequently protected with the semi-ipln and 380 microns for those tested without damage protection on top.

The electrical requirements for each cell of the cathodic disbondment test were provided by an Amel Instruments general purpose potentiostat model 2049. Four cells were run simultaneously and wired to a PC. Special glass cells were made for these high temperature tests. The cells, one of them shown in Figure 9, can be sealed against the coated coupon by means of an O-ring/clamp system. No sealant or caulk is needed. The O-ring is capable of continuous use temperatures up to 240°C. The glass vessel is equipped with coils where a hot/cold liquid circulates to condition the temperature of the electrolyte. There are four ports on top of the glass vessel. They accommodate a water cooled condenser (to reflux the liquid back into the vessel), a Teflon™ coated temperature probe (to measure the temperature of the liquid near the coating's surface), a platinum and a calomel electrode (rated for 100°C). The head space of the glass vessel is large enough to accommodate vigorous boiling in the electrolyte solution. The coated sample is heated from below by means of a digital hot plate (Omega LHS series data/plate). The temperature at the lower surface of the coated coupon is monitored by two sensors forced to contact the metal directly by means of a spring, see Figure 10.

One sensor sends a signal to be recorded in the computer and the other is a feedback to the hot plate controls. Custom made software controlled the tests and recorded the data. The tests ran for 672 hours. Recorded continuously were: temperature of the lower part of the coupon (inner surface of pipe), temperature of the solution near the coating's surface (medium surrounding pipe), voltage (kept at 1.5 V), and current in milliamps.

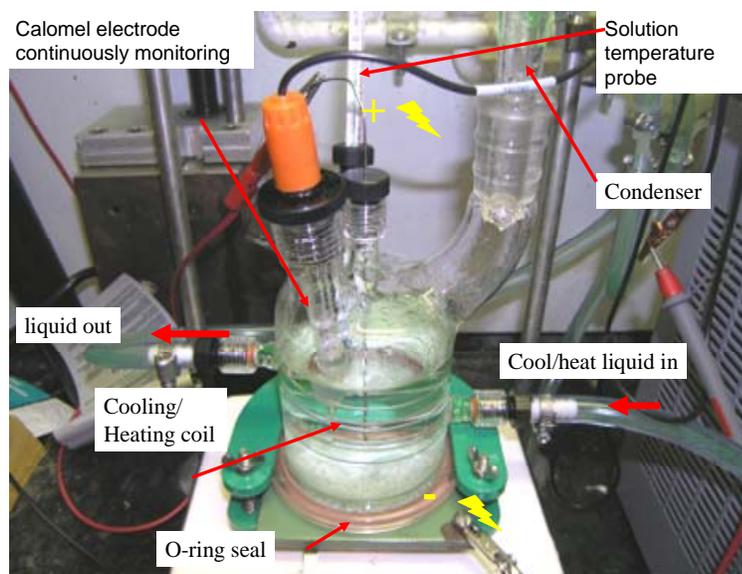


Figure 9. High temperature cathodic disbondment cell.

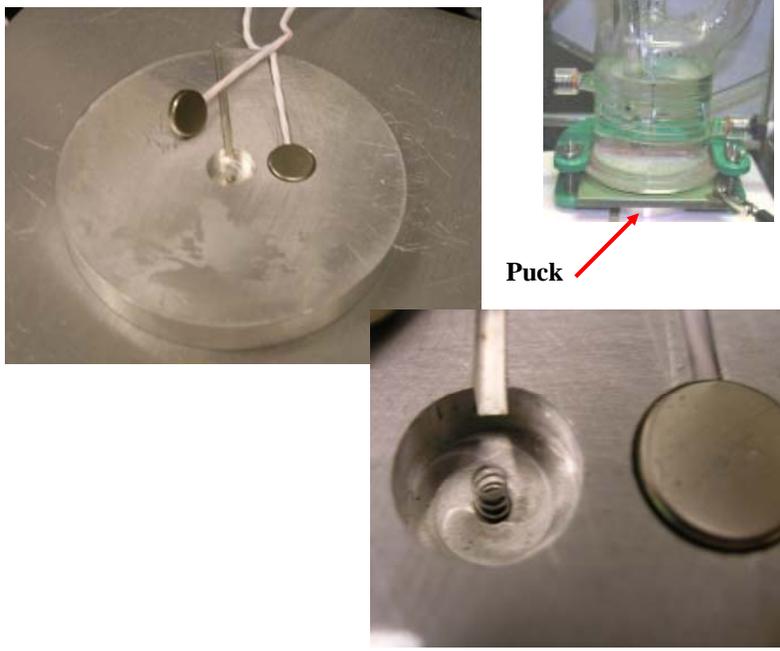


Figure 10. Aluminum puck between hot plate and sample, one thermocouple provides feedback to the hot plate and the other signal goes to the computer.

Figures 11 and 12 show the recorded data for a couple of tests: voltage, current, in addition to the metal and solution temperatures. The holiday diameter was 3.2 mm (1/8 of an inch). All holidays were drilled to the same metal depth in order to keep a similar reaction area for all the tested samples. The 3% by weight salt solution was prepared using deionized water and reagent grade NaCl (J.T.Baker). The software sends 24 hour and 2 hour warnings that the test will end. Once the test panels were removed from the testing apparatus, they were sliced and pried using a utility knife. An average and a standard deviation were computed from the 8 measured slices. Measurements were made from the holiday's periphery to the start of the radial cut using a digital caliper.

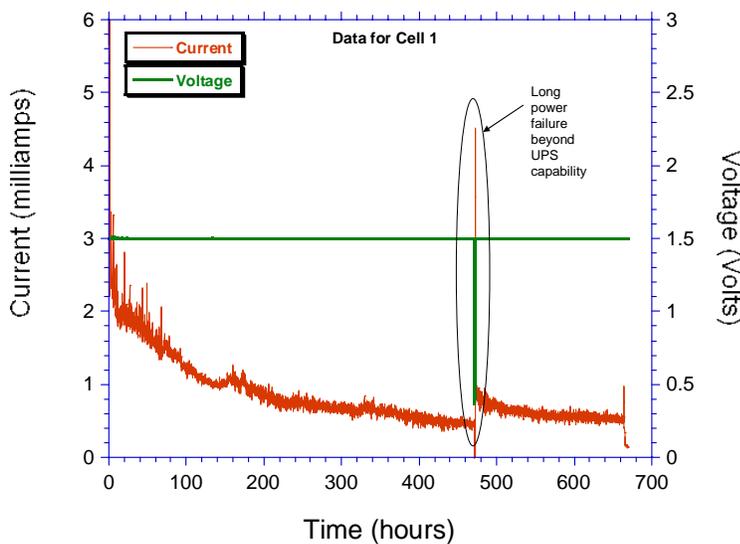


Figure 11. Current and voltage data for cell 1 of a high temperature cathodic disbondment apparatus.

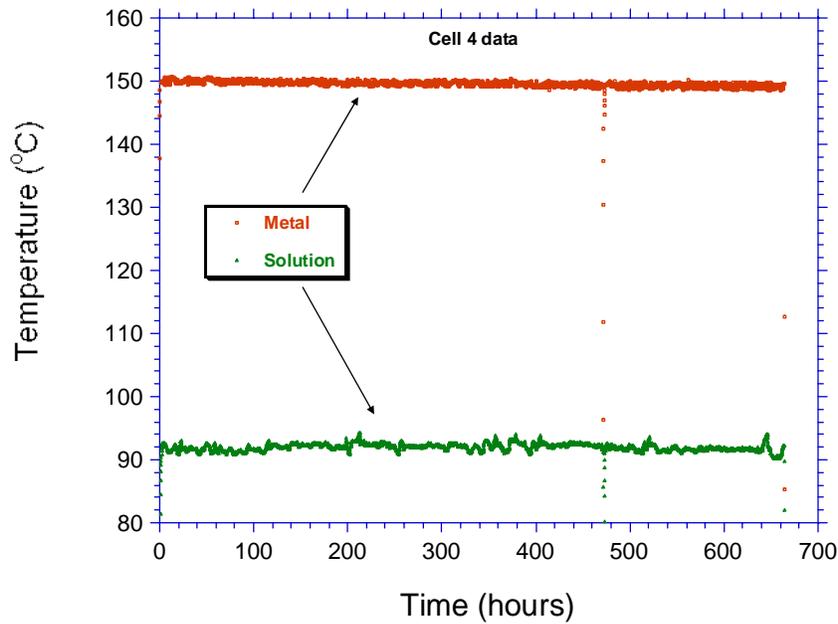


Figure 12. Temperature data for Cell 4 of a high temperature cathodic disbondment apparatus.

Tested specimens and their recorded data are shown in Figure 13.

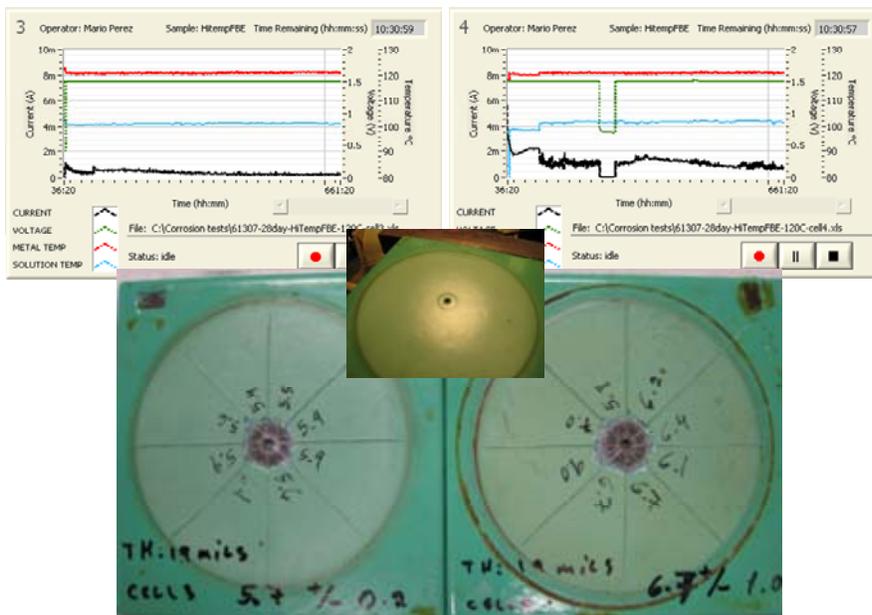


Figure 13. 28 day cathodic disbondment data for experimental high temperature fusion bonded epoxy at a metal temperature of 120°C and a solution temperature of 100°C.

A simple Excel calculation of multilayer coating interface temperatures and overall heat transfer of these coatings is shown in Figure 14. The equations utilized for this two dimensional rectangular coordinate analysis are shown below.²²

$$Q = - \frac{T_{\text{overall}}}{\frac{\Delta X_{\text{steel}}}{k_{\text{steel}} A_{\text{steel}}} + \frac{\Delta X_{\text{fbe}}}{k_{\text{fbe}} A_{\text{fbe}}} + \frac{\Delta X_{\text{pnc}}}{k_{\text{pnc}} A_{\text{pnc}}} + \frac{1}{h_{\text{rl}} A_{\text{rl}}}} \quad (1)$$

$$T_{\text{steel}} = Q \left(\frac{\Delta X_{\text{steel}}}{k_{\text{steel}} A_{\text{steel}}} \right) + T_{\text{hotplate}} \quad (2)$$

$$T_{\text{fbe}} = Q \left(\frac{\Delta X_{\text{fbe}}}{k_{\text{fbe}} A_{\text{fbe}}} \right) + T_{\text{steel}} \quad (3)$$

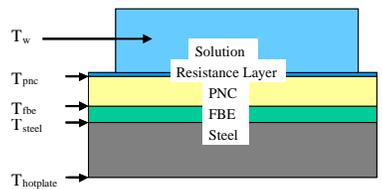
$$T_{\text{pnc}} = Q \left(\frac{\Delta X_{\text{pnc}}}{k_{\text{pnc}} A_{\text{pnc}}} \right) + T_{\text{fbe}} \quad (4)$$

$$T_{\text{overall}} = T_{\text{hotplate}} - T_{\text{water}} \quad (5)$$

CALCULATION OF INTERFACE TEMPERATURES FOR MULTILAYER COATINGS: CD TEST OR SMALL SECTION OF LARGE DIAMETER PIPE

Instructions: enter (yellow cells) layer thickness, hot plate temp (C15), steady state aqueous medium temp (C16). **Questions:** Mario Perez (651) 736-0331
 Thickness X = layer thickness (m), k = thermal conductivity (W/mK), h = heat transfer coefficient, in this case that of the resistance layer (W/m2K), A= heat transfer area (m2), T=temperature (K), Q = heat flow or load (W).

INPUTS		
Xpnc	0.000508	20
Xfbe	0.000203	8
Xsteel	0.005994	236
ksteel	45	
kfbe	0.84	
kpnc	0.21	
h (reslayer)	2300	
Asteel	0.010323	
Afbe	0.010323	
Apnc	0.010323	Temp
A (reslayer)	0.00535	(Celsius)
Thp (hot plate temp)	423.15	150
Tw (water)	373.15	100



CALCULATIONS:		
Q	-142.0645	
Tsteel	421.3167	148.17
Tfbe	417.99	144.84
Tpnc	384.70	111.55
Delta T steel	-1.83	
Delta T fbe	-3.33	
Delta T pnc	-33.29	
Delta T res layer	-11.55	
Delta T total	50.00	

CALCULATION CHECK:
 Delta T total: 50

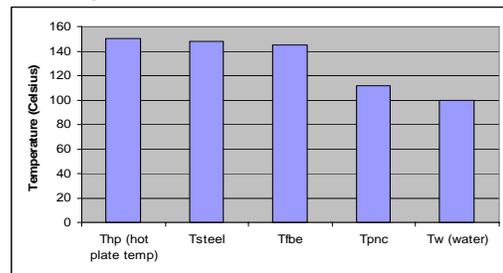


Figure 14. Spreadsheet for the calculation of interfacial temperatures in multilayer coatings.

Results. Peel tests. The results for the 180-degree peel tests are shown in Figure 15 below.

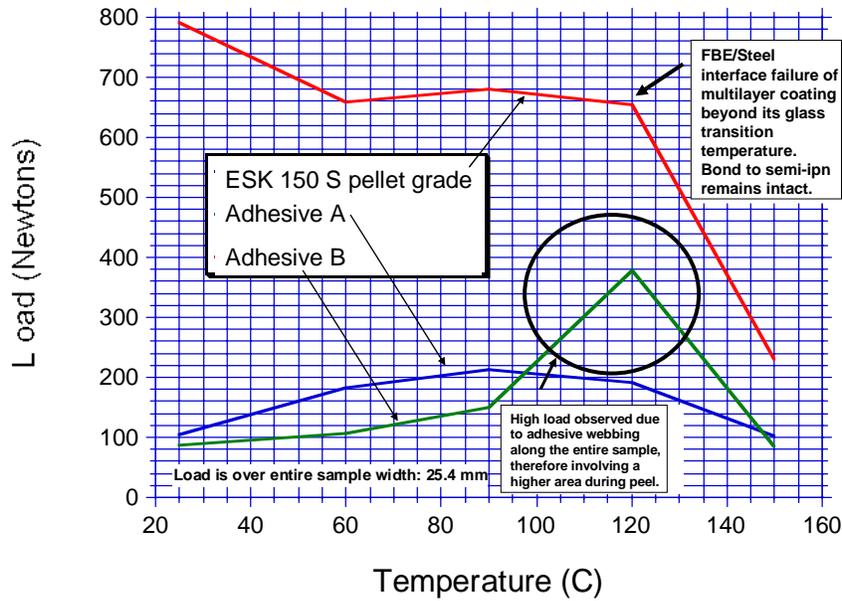


Figure 15 180-Degree Peel Load as a Function of Temperature for Various Adhesives.

It can be observed that the interpenetrating network shows higher adhesive power than the two polypropylene adhesives at any of the temperatures tested. Due to the glass transition temperature of the fusion bonded epoxy utilized for this trial, those samples adhered with the semi-ipn failed at the FBE/steel interface at 120°C and 150°C. A recent study of 3-layer (FBE/adhesive/pp) coatings reported values for the peel adhesion of the adhesive/FBE interface at 107°C to range between 7 and 65 N/mm²³. Our data shows the functionalized olefin adhesives closer to the lower range reported in this paper for the reasons mentioned above of trying to adhere to an already cured fusion bonded epoxy surface. Tested specimens are shown in Figure 16.



Figure 16. Peeled Specimens from left to right: Adhesive A, Adhesive B, powder semi-ipn, Pellet semi-ipn. Cohesive failure on SEMI-IPN S, adhesive failure for adhesives A and B.

It can be noted that the linear functionalized olefin adhesives (A and B) failed adhesively from the fusion bonded epoxy surface, while the semi-ipns failed cohesively due to their aggressive bonding to the cured epoxy resin.

Cathodic Disbondment. Similar cathodic disbondment results were obtained for the 28 day tests of the experimental high temperature fusion bonded epoxy for metal temperatures above 100°C. This was previously shown above in Figure 13 and below in Figure 17. The disbondment radii at 120°C were 5.7 +/- 0.2 mm and 6.7 +/- 1.0 mm. Those at 140°C were 6.6 +/- 0.4 mm and 8.7 +/- 2.0 mm. The only significant difference shown in this latter figure was that a relatively thin layer of semi-ipn improved the cathodic disbondment protection provided by the fusion bonded epoxy. The cathodic disbondment radius for this case was 4.6 +/- 0.1 mm. This may be due to the very strong bond between the semi-ipn and the fusion bonded epoxy and the barrier properties of the semi-ipn. Future experiments with this high temperature device will attempt to elucidate effects observed by changing either solution and/or metal temperatures.

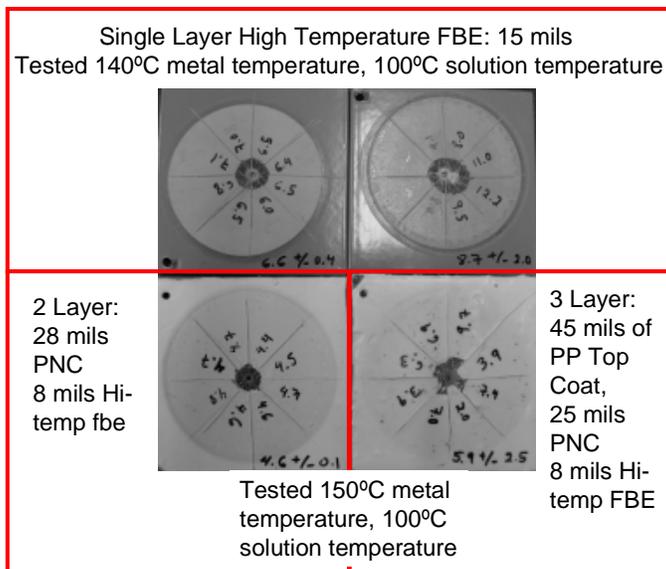


Figure 17. 28 day cathodic disbondment tests for new high temperature materials

CONCLUSIONS

This paper provided an overview of performance properties required of a high-temperature pipe coating and a review of test methods designed to predict the functional life of a coating. Using typical industry test methods it also showed a comparison between a commercially available FBE and examples of high-temperature FBE coating materials. It also introduced a new technology for the adhesive tie-layer used in three-layer PP systems for high temperature use. Finally, it provided new experimental test procedures that may be useful in the development of new generation coatings.

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