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## Accelerated Aging of Fusion Bonded Epoxy Coatings Juliana Francisco<sup>a</sup>, Fabio Aguirre<sup>b</sup>, Don Kirkpatrick<sup>c</sup>

### Abstract

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Fusion Bonded Epoxy (FBE) coatings have been successfully used for several decades to protect oil and gas pipelines from corrosion. A relatively recent industry trend is the increase in pipeline design temperatures, which has triggered the development of new high glass transition temperature (T<sub>g</sub>) FBE coatings. Nevertheless, the long term performance of the FBEs at these increasingly higher operating temperatures is not well understood. Accelerated aging at higher temperatures than the operation temperature coupled with extrapolation is typically employed to predict the service life of FBE coatings, however this approach assumes that the aging mechanism at high temperatures is the same as it is at the actual service temperature of the coating, which is unlikely to be the case. Our proposed approach for determining the service life of FBE coatings is to accelerate aging using increased oxygen concentration allowing data collection in a reasonable time at different temperature set points. This could prove to be a more valid method to predict service life of FBE coatings. Also, in the current work, we will determine whether the thermal degradation mechanism varies with FBE formulation and temperature, as well as whether high T<sub>g</sub> FBEs appear more thermally stable at the intended service temperature.

**Keywords:** FBE, glass transition temperature, thermal aging

### Introduction

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Fusion Bonded Epoxy (FBE) coatings have been successfully used for several decades to protect oil and gas pipelines from corrosion. A relatively recent industry trend is the increase in pipeline design temperatures, which has triggered the development of new high glass transition temperature (T<sub>g</sub>) FBE coatings. Nevertheless, the long term performance of the FBEs at these increasingly higher operating temperatures is not well understood. In an effort to predict the long term durability of coatings, the industry (1-3) has been using extrapolation techniques from temperatures much higher than the actual service temperature of the pipeline since direct quantification of FBE long term corrosion protection at use temperature can be prohibitively slow.

To shorten the experimental time, the coatings aging is accelerated with higher temperatures and then the Arrhenius model is used to predict lower temperature behavior. For FBEs this would involve collecting data above its T<sub>g</sub> and extrapolating through the T<sub>g</sub> to the service temperature. Unfortunately no studies exist testing the validity of this extrapolation method for FBEs. Many potential issues exist in accelerated aging itself and in the extrapolation of

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the data. For polymer degradation, implicit in the validity of the extrapolation is the assumption that the degradation mechanism during the testing is the same as in service, only faster. Another common assumption is that the quantity measured, weight loss for example, correlates well with the corrosion protection properties of the coating.

Another approach used to accelerate the rates of thermo oxidation is to increase the concentration of oxygen. If the kinetic model is known, it can be valid to extrapolate the absolute rates from high to low concentrations using the kinetic expression. In the current work we report the validity of increased oxygen concentration to accelerate data collection. Higher oxygen concentrations can be achieved at atmospheric pressure by utilizing greater than 21 % in volume of oxygen, increased air pressure or some combination of these. Although until now, this enhanced oxidation rate technique has not yet been reported for FBEs, it has shown applicability to a broad range of materials including lead (4), vegetable oil (5), mineral oil (6), an inorganic thermal barrier coating (7), polypropylene (8) ethylene propylene rubber (9) and cured epoxy polymers (10-13). Often when reported, the kinetics of oxidation are first order with respect to oxygen concentration (8, 11, 14). One of the typical methods frequently used for monitoring polymer degradation is simply quantifying weight loss of exposed samples over time. As the polymer chains are broken, it can result in species of sufficiently low molecular weight to volatilize from the polymer at the exposure temperature. We used this gravimetric technique in this study since it seems reasonable to correlate reduction in mass with decreased corrosion protection. However, how much coating mass loss is needed to affect corrosion protection and whether other properties of the coating are more relevant remains to be quantified.

In the current work, we will determine whether the thermal degradation mechanism varies with FBE formulation and temperature, as well as whether high T<sub>g</sub> FBEs appear more thermally stable at the intended service temperature.

## Methodology

The oxygen exposure at above ambient temperature was accomplished in pressure vessels placed in laboratory ovens. Compressed air was the gas used. The pressures were 0 kPa, 5.2 kPa (75 PSIG) and 1034.2 kPa (150 PSIG). The temperatures were 130 °C and 180 °C. The service temperature of the coating was assumed to be 130 °C, which is between 20 °C to 30 °C below the T<sub>g</sub> of the high T<sub>g</sub> FBE films and 20 °C above the T<sub>g</sub> of the standard FBE film used in this study.

Using the ideal gas law to calculate O<sub>2</sub> concentrations at the appropriate temperatures yields the results in Table 1.

**Table 1 - Oxygen concentrations calculated from gauge pressure and ideal gas law**

| Air<br>pressure<br>(kPa)             | Temperature (°C) |        |        |
|--------------------------------------|------------------|--------|--------|
|                                      | 23               | 130    | 180    |
| O <sub>2</sub> concentration (mol/L) |                  |        |        |
| 0                                    | 0.0088           | 0.0065 | 0.0057 |
| 5.2                                  | 0.0537           | 0.0394 | 0.0351 |
| 1034.2                               | 0.0985           | 0.0724 | 0.0644 |

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The FBE free films were placed into the heated vessels and the pressure increased to the desired level. The two sides of the free films were exposed to the air and release of low molecular weight degradation products would be from two sides, unlike testing a coating which would have only one free surface. In addition, thus far high Tg FBE coatings are used as primers in multilayer systems on flow assurance pipelines and hence they are not directly exposed to the environment. If diffusion rate of the degradation products through the FBE is comparable or slower than their rate of production, weight loss from free films compared to a coating of the same thickness would be different. One way to determine whether diffusion rate has significant influence on weight lost rate would be to evaluate samples of different thickness. However, in this work thickness variation was minimized in order to make valid comparisons between samples and temperatures in the event diffusion was relevant to the measured weight loss rate.

The pressure vessels were about 11.4 L (3 gal) capacity each and constructed of stainless steel. Removable shelves allowed the samples to be quickly placed into and removed from the vessels. They were pressurized using regulated compressed air cylinders. Since the samples would slowly consume oxygen, a small flow through the vessels was needed to assure the O<sub>2</sub> partial pressure remained constant over time. This was accomplished using a small leak of about 20 cm<sup>3</sup>/min of air measured at atmospheric pressure. This included the vessel held at atmospheric pressure.

The free films were prepared by attaching a 75 mm by 150 mm sheet of thick aluminum foil coated with a silicone thermoset release coating onto a steel panel of dimensions 3 mm x 75 mm x 200 mm, pre-heating this panel in a convection oven set at 240 °C for 30 min, then placing it in a fluidized bed containing the powder coating. The coated panel was then immediately placed in an oven at 240 °C for 2 min to cure the coating. After curing, the panel was quickly quenched in a water bath at ambient temperature for 2 min, and then the FBE film was removed from the foil.

Although it is recommended to use thicker coatings for high service temperatures, in this study the samples were about 300 µm (12 mils) thick with initial weight of about 0.5 g. The exposure of the films was as follows. Samples were stored in a desiccator for 3 weeks to draw off most moisture. The initial weights were then taken. The vessels were equilibrated to the appropriate temperatures at atmospheric pressure. The samples were placed on aluminum foil that had a cured silicone release coating. The foils containing the samples were placed into the vessels which were then closed and brought to pressure. For tracking the weight over time, the vessels were de pressurized, the samples were quickly removed, weighed, placed back into the vessels, and re pressurized. Three samples each were tested and the average is reported.

The FBE films used in this study were as follows:

FBE 1: FBE film with a cured Tg of 105 °C, based on a standard 4-type epoxy resin cured with a standard phenolic hardener

FBE 2: High Tg, FBE film with a cured Tg of 163 °C, based on a specialty epoxy resin cured with a specialty phenolic hardener

FBE 3: High Tg, FBE film with a cured Tg of 163 °C based on a specialty epoxy resin cured with dicyandiamide (DICY)

All the above FBE films contain 10 % extender volume concentration.

These FBE films were prepared for this particular study with a minimum number of formulation ingredients to reduce potential confounding effects. Results using fully optimized FBE coatings might be different than presented here.

## Results and discussion

The data for weight loss at 180 °C at the three air pressures for FBE 3 is given in Figure 1. Except for the very early data, the change in weight versus time appears to be linear and the weight loss rate increases with O<sub>2</sub> pressure,

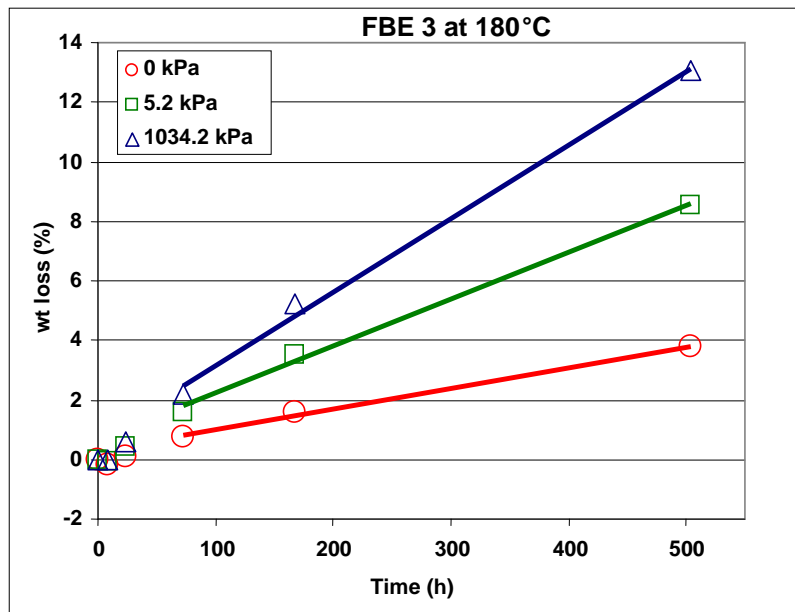


Figure 1 – 180 °C weight loss data from exposure at various air pressures over time.

The line fit to the later data does not intercept the origin. There is a finite y intercept, caused by a very small but rapid weight loss between time zero and when the first few data points are taken. We interpret this as either small molecules present initially in the sample and/or the initial step in the epoxy polymer oxidation, that of chemical dehydration (15-16). For example, it could simply be more tightly bound water in the extender that was not removed by the desiccant at room temperature. After this initial small but rapid weight loss, the slopes in Figure 1 are linear; yielding a single weight loss rate for this time interval at each pressure quantified by the slope.

The data for weight loss at 130 °C at the three air pressures for FBE 3 is given in Figure 2. Note the time scale difference compared to the 180 °C data of Figure 1. It appears the data between time 0 and 1500 h shows some randomness. In fact, at 5.2 kPa (75 PSIG) and 1034.2 kPa (150 PSIG), a very small initial weight gain is apparent.

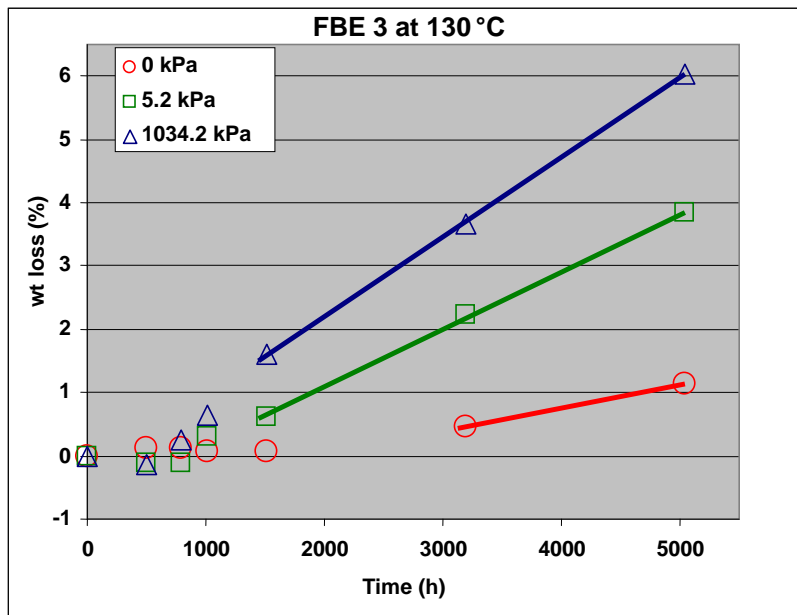


Figure 2 – 130 °C weight loss data from exposure at various air pressures over time.

We interpret this as a result of the thermo oxidative process, which occurs by oxygen reacting with the polymer chains, creating oxygen containing species while breaking the chains. Initially the cured epoxy polymers are highly cross linked and thus a small amount of random chain breaks will not produce sufficiently small molecules which can volatilize. Once enough bonds are broken to create low molecular weight species, mass loss proceeds. In some of the early data of weight loss vs. time shown in Figure 2 small positive weight gains can be seen. Apparently this is the result of adding the oxygen mass to the chain. After this time interval the weight loss vs. time becomes linear like that seen in the 180 °C data. The linear weight loss rates were quantified using this data but for only the last few data points.

If the rate of oxidation as measured by weight loss rate is proportional to oxygen concentration, a linear correlation of weight loss rate with oxygen concentration should be observed. The graph of these slopes, the % weight loss per hour, is given in Figure 3 for FBEs 1, 2 & 3.

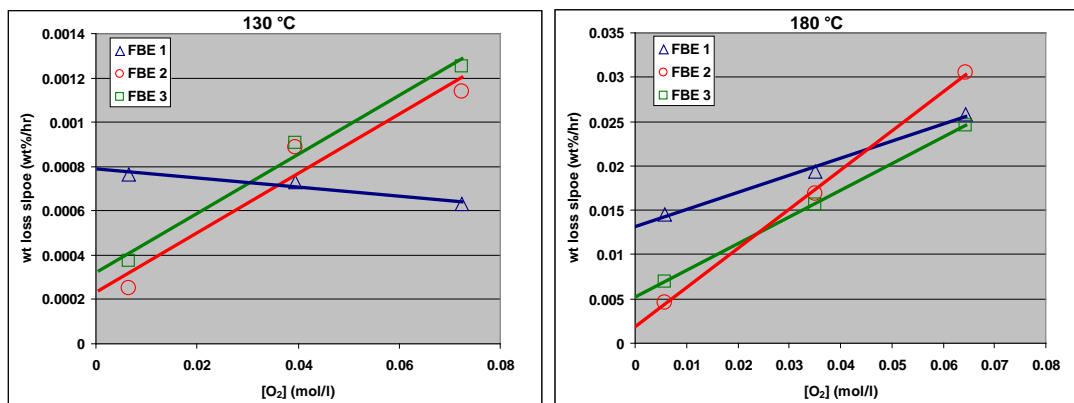


Figure 3 - Weight loss/time vs. O<sub>2</sub> concentration for the three FBEs at 130 °C and 180 °C.

The linear fit is good showing that the weight loss rate is proportional to oxygen concentration and confirming the first order dependence found in the previous literature.

However the behavior of FBE 1 was unexpected. The relatively significant y intercept suggests a rapid non-oxidative weight loss mechanism simultaneous with the oxidative process. In addition, at 130 °C FBE 1 shows a small decrease in weight loss rate with oxygen concentration.

The non-oxidative process is relatively significant for all of the FBE films used in this study even at 130 °C, which is rather surprising since a literature review of epoxy oxidation (17) reveals that for most cured epoxy resins studied (typically composite formulations and not coatings) it is generally thought that the oxidative processes predominates below 200 °C and non oxidative processes become more significant above this temperature. For example Ciutacu (12) et al, gives data for decrease in flexural modulus of an epoxy composite over time for two oxygen pressures at 125 °C and 145 °C. From this data, rate of change per time vs. O<sub>2</sub> concentration can be plotted to illustrate the relative significance between oxidative and non oxidative processes for this epoxy composite formulation. This is shown in Figure 4.

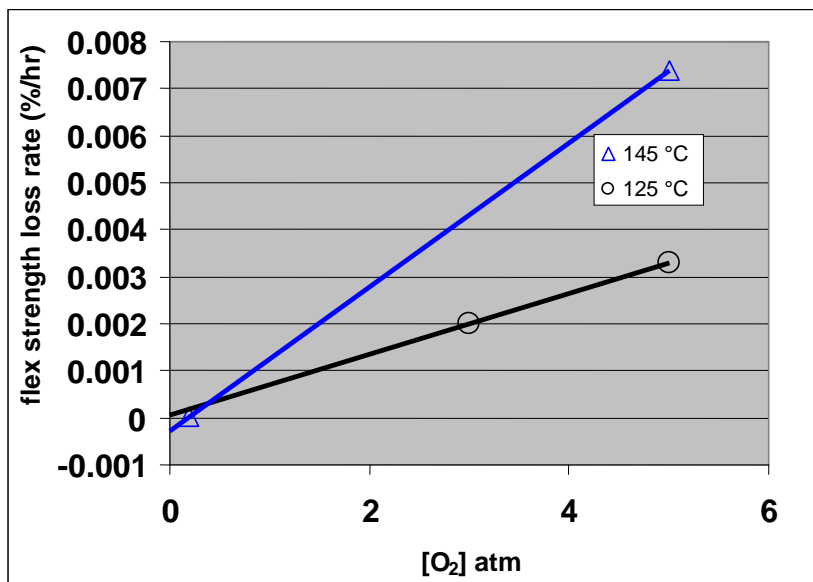
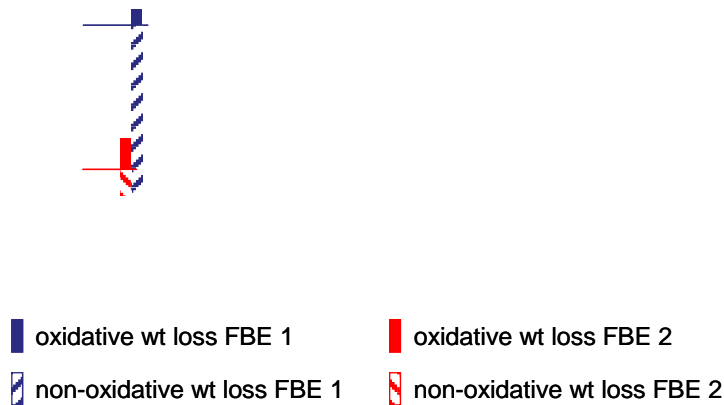


Figure 4 - Graph drawn from data of Ciutacu(12) showing the influence of O<sub>2</sub> concentration on rate of flex modulus loss for oxidation of epoxy composite.

At both temperatures, the rate of flexural strength reduction appears first order with oxygen concentration. In the timeframe of the experiment, little if any non-oxidative process is observed, as indicated by a y intercept very close to 0. If a non oxidative process had significant influence on decreasing flexural modulus, a positive y intercept should be observed.

Atmospheric concentration of oxygen (0 kPa air) is a pertinent condition to make a comparison of the relative oxidative and non oxidative degradation rates. This condition is the first data point shown in the O<sub>2</sub> concentration vs weight loss rate graphs. Take for example both FBE 1 and FBE 2 at 180 °C. The bars drawn in Figure 5 show the relative comparison

of oxidative and non-oxidative weight loss rates for these two FBE films. The striped bars represent the non-oxidative loss rate and the solid bars represent the oxidative rate. The ratio of oxidative to non-oxidative weight loss rate is very different between these two formulations. At 1 atm air pressure, FBE 1 is obviously losing weight at a much faster overall rate than FBE 2, yet FBE 2 is oxidizing slightly faster than FBE 1. The much higher non-oxidative mass loss rate of FBE 1 is what contributes to its overall faster weight loss rate compared to FBE 2.



**Figure 5 - Oxidative and non-oxidative rate comparison of FBEs 1 and 2 at 180 °C.**

Therefore, although the degradation is first order with oxygen concentration, it cannot entirely describe the degradation rate. Increasing oxygen concentration will only accelerate a portion of the overall degradation but will not increase the non-oxidative portion shown by the y intercepts of Figure 3.

These mass loss measurements demonstrate the complexity in the thermal degradation mechanisms of these cured FBE films. Not only is it shown that both non-oxidative and oxidative rates can be significant, but like in the case of FBE 1 at 130 °C, it actually indicates a decrease in overall degradation rate with oxygen concentration. This sample at this temperature also had the highest ratio of non-oxidative vs. oxidative weight loss rates. It seems counterintuitive that the oxidative component of mass loss would decrease with higher oxygen concentration. However, one explanation for this would be that the oxidative weight loss rate actually does increase with oxygen concentration, but the oxygen is also involved in quenching the non-oxidative component making the total observed slope downward with higher oxygen level. This same process might be occurring in the other samples and temperatures, it is just not as apparent since the overall degradation rate increases with oxygen concentration.



The quantitative response to temperature and oxygen concentration reported here is most likely not representative of all FBEs as these were free film formulations, purposefully designed with few components to minimize potential confounding effects of commonly used additives. The behavior could also be different among commercial coatings due to variances in formulation and cure conditions. In addition, if diffusion plays a role in the weight loss process, free films versus coatings would affect behavior as would the thickness of the test samples.

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## Conclusions

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- In the range of service temperatures for oil and gas pipelines, both oxidative and non-oxidative mechanisms can be significant in thermal aging of FBEs.
- The balance between oxidative and non-oxidative degradation rates of FBEs is dependent on the formulation and temperature.
- This O<sub>2</sub> concentration technique can separately quantify the oxidative and non-oxidative wt. loss rates.
- Oxidation of FBEs appears first order in O<sub>2</sub> concentration.
- Extrapolation of the thermal oxidative rate to longer times by using data collection accelerated by increased O<sub>2</sub> concentration is valid, but only for the oxidative portion of the degradation.
- We have demonstrated that the standard FBE film studied here degrades faster, as quantified by mass loss at the intended service temperature of 130 °C compared to the high T<sub>g</sub> FBE films.
- It appears the mass loss rate for the standard FBE formulation studied here is predominately non-oxidative.
- At 1 atm air pressure and both 130 °C and 180 °C, FBE 2 cured with a multifunctional phenolic hardener yielded greater thermal stability than FBE 3 cured with DICY. This is consistent with previous studies that suggest the use of phenolic hardeners improve the thermal stability of cured epoxy polymers.

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## References

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- (1) M. Batallas, Corrosion 2008, Paper 08039
- (2) J. A. Kehr et al, Corrosion 2008, Paper 08040
- (3) V. Boerschel. Corrosion 2010, Paper 10012
- (4) N. Bagshaw, et al, British Corrosion J., 4(6), 301 (1969)
- (5) B. Kowalski, European J. of Lipid Sci. and Tech., 106(3), 165 (2004)
- (6) Li, J. of Canadian Petroleum Tech., 45(1), 48 (2006)
- (7) C. Zhang, et al., Surface & Coatings Tech., 201, 446 (2006)
- (8) L. Achimsky, et al., Eur. Polym. J., 35, 557 (1999)
- (9) S. Ciutacu et al., Polym. Deg. Stab., 29, 321 (1990)
- (10) T. Tsotsis et al., Polym. Deg. Stab., 64, 207 (1999)
- (11) H. LeHuy, et al., Polym. Deg. Stab., 35, 171 (1992)



- (12) S. Ciutacu, et al., Polym. Deg. Stab., 31, 365 (1991)
- (13) Decelle et al, Polym. Deg. & Stab., 81, 239 (2003)
- (14) H. Sohn & S. Kim, Ind. Eng. Process Des. Dev., 19, 550 (1980)
- (15) Paterson-Jones, J. Appl. Polym. Sci., 19(6), 1539 (1975)
- (16) Lee, J. Poly. Sci., Part A, 3(3), 859-882 (1965)
- (17) D. Kirkpatrick et al., Corrosion 2008, paper 08037