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# Three layer polyolefin coatings: how the FBE primer properties govern the long term adhesion

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## ABSTRACT

Loss of adhesion has been identified on pipelines coated with three layer polyolefin coatings (3LPO) over the past few years. This study was launched by TOTAL to correlate the wet behaviour of commercial fusion bonded epoxy (FBE) primers to the long-term adhesion of related 3LPO systems aged in water. The first part of this paper examines the water uptake behaviour of six FBE grades (free standing films and coatings), and characterises their wet Tg and adhesion. The second part of this paper investigates the long-term adhesion of plant applied 3LPO and related bilayer systems (3LPO without top coat to accelerate the water permeation to sublayers). Adhesion and durability of FBE materials in a wet environment are pointed out as key factors governing the long term adhesion of 3LPO systems.

## 1 BACKGROUND

Polymeric coatings are being used classically for external pipeline protection in the oil and gas industries over years in complement to cathodic protection (CP). The direct benefit of the use of organic coatings impairing good barrier properties in addition to the cathodic protection is the resulting low demand in CP current.

### 1.1 Conditions for sustainable coating barrier properties

Let first summarise the main parameters governing the performance of an organic coating barrier.

i) The quality of steel surface preparation and coating application are key parameters influencing both short and long term coating performances [1, 2]. Steel preparation

includes metal grit-blasting to a given physical roughness (enhanced FBE wettability and anchoring to steel) and degree of cleanliness ensuring that there are no rust nor polluting species (dust, salts...) remaining on the surface.

ii) The coating application is critical to avoid defects in the coating (porosity or inhomogeneous coating thickness with areas with thinner coating) but also to offer proper cure and post-cure conditions for the reacting polymers prior to final quenching.

iii) The ability of coatings to withstand damage is also an important property because it will affect the number of coating defects [3]. Mechanical damages may be hazardous (due to pipe transportation, installation or inspection) but can also affect a pipe in service (tool penetration).

iv) The permeability of corrosive species (water, oxygen, ions) through the organic coating is another key factor governing its corrosion protection ability [4, 5]. However it is not systematically evaluated in service conditions since it is not part of classical prequalification tests. Mathematically the permeability is defined by [6]:

$$Pe = D \times S \quad (\text{equation 1})$$

where Pe, D and S are, respectively, coefficients of permeability (in  $\text{m}^2 \cdot \text{Pa}^{-1} \cdot \text{s}^{-1}$ ), diffusion (in  $\text{m}^2 \cdot \text{s}^{-1}$ ) and solubility (in  $\text{m}^3 \cdot \text{m}^{-3} \cdot \text{Pa}^{-1}$ ).

The permeation flux through an organic coating is proportional to the permeability and inversely proportional to the coating thickness (in the case of a classical diffusion behaviour modelled with a Fick law). In a general way, the permeability of small molecules through polymers is an intrinsic property and varies with the nature of penetrant and polymer, reflecting its molecular structure and the potential degree of interaction between molecules and polymer chains [7]. Note that diffusion process is thermally activated (temperature dependence modelled with the Arrhenius law), therefore permeability also depends on the operating conditions.

v) Differential swelling between steel pipe and coating due to polymer plasticization by water could be detrimental for the long term adhesion of the coating to the metal. This phenomenon is a consequence of the coating permeability towards water and may be enhanced by temperature cycling.

vi) The chemical resistance of the outer coating material to its external environment is obviously a critical factor. In case of multilayer coatings, the durability of sub-layer materials and interfacial boundaries to steel in the presence of permeating molecules may also play a key role in the coating long-term efficiency and was not particularly investigated so far. The durability of a polymer under given environmental conditions is an intrinsic property depending on the chemical composition, e.g. some chemical functions such as dicyandiamines are prone to hydrolysis in the presence of water above  $60^\circ\text{C}$  [8]. Hence for multilayer coatings, hydrolysis could occur in sub-layers as soon as water has permeated through the top-coat, even undefectuous.

## 1.2 Disbonding of 3LPO coatings

Three-layer polyolefin systems feature:

- an epoxy primer layer (Fusion Bonded Epoxy) providing both adhesion and corrosion protection to steel,
- an adhesive tie layer,
- a polyolefin outer layer (polyethylene or polypropylene). This top-coat offers outstanding mechanical resistance to damage occurring during both pipe manufacture and installation.

As a consequence, such multi-layer coatings are supposed to provide efficient and sustainable corrosion protection to the pipe steel over 20 years service or more, including exposition to humidity and temperature (cycling conditions). However, loss of adhesion has been identified over the past few years on pipelines coated with 3LPO systems exhibiting no defect [9, 10]. Since polyolefins have a very large electric resistance, they can lead to shielding of the cathodic protection, when the coating is disbanded and presents no macroscopic defect for the current flow, especially in onshore applications with a low conductivity environment (soils). Corrosion risks under disbanded coatings urges the need for a better understanding of the degradation mechanisms resulting in the poor adhesion of the FBE primer layer to the pipe steel.

A first study launched by IFP on tube sections industrially coated with 3LPO systems has pointed out that the water permeability of an undefectuous polyethylene top-coat does not prevent the water ingress into sub-layers (adhesive and primer ones) within a few months time, depending on the internal temperature [11, 12]. Experimental results were in good agreement with unidirectional modelling of the water permeation at 60°C and 20°C, showing that the saturation level in the FBE primer could be reached after one and two years, respectively [13]. Effects of polyolefin permeability to water were fully highlighted because they were not superimposed to classical disbonding phenomena occurring on scarified coating, due to water interfacial diffusion and cathodic protection. As main consequences of the water permeation through the top-coat material, the adhesion to steel measured by peeling tests was significantly diminished. Bilayer systems (3LPO without top-coat) applied on tubes in similar conditions were also aged and peeled at the same time. This method revealed as an efficient accelerated test since the time of water diffusion through the polyolefin top-coat is saved.

### **1.3 Specific methodology**

Previous studies aforementioned were performed with a unique FBE grade, thus the influence of the primer properties on the adhesion performance of 3LPO coatings was not discussed yet. The objective of the present study is to correlate the long-term adhesion of related 3LPO systems, plant applied on steel tubes and aged in water at both room and maximum operating temperatures to the wet properties of commercial FBE materials. Attention will be paid to:

- The glass transition temperature ( $T_g$ ) in the wet state, referred as wet  $T_g$ , lower than the dry  $T_g$  due to FBE plasticization by water molecules. The glass transition between a glassy state ( $T < T_g$ ) to a rubber state ( $T > T_g$  for thermosets) can be explained at the molecular scale by the development of generalised cooperative chain motions above  $T_g$ , whereas chain mobility remains local below  $T_g$ . The glass transition has very important practical consequences for FBE coatings, such as a significant drop of the Young modulus from glassy to rubber state which can explain the loss of adhesion classically observed in the dry state by increasing the temperature in the vicinity of  $T_g$  or following immersion [14]. Another main consequence is the electrical behaviour of epoxies, capacitive below  $T_g$  becoming conductive above  $T_g$  which favours corrosion. Indeed, there are ionic species within epoxy materials remaining from monomer synthesis [15]. Hence it is of main interest for FBE coatings to determine the wet  $T_g$  and to define the upper temperature limit sufficiently below this value to keep FBE glassy in service.
- The durability in the wet state since water entrance in FBE coatings favours differential swelling between polymer and metal and may cause hydrolysis, given the chemical nature of FBE and the operating conditions. In turn, polymer hydrolysis can induce osmotic blistering according to mechanisms well described

in the literature, where water is continuously entering due to differing osmotic pressure between external and internal media. Hence, it is of main interest to study the long-term water uptake of FBE materials at ambient and maximum service temperatures to reveal unsuitable swelling or hydrolysis phenomena through abnormal behaviours (e.g. non stabilised water uptake).

The first part of this paper examines the long-term water uptake behaviour of six commercial FBE taken as free standing films and applied as coatings to steel plates, and characterises the FBE physico-chemical properties such as the wet T<sub>g</sub> and the adhesion after one week and three months immersion in water. Results obtained after ageing are compared to initial properties and discussed. Among the tested FBE grades, two were selected for their differing behaviours towards water and were plant applied on tubes as primers in complete 3LPO systems and related bilayer systems. Laboratory evaluation of the long-term adhesion during ageing were performed on both 3LPO and bilayer systems. The influence of intrinsic FBE properties on the bonding strength measured on tubes during ageing is discussed in the second part of the paper.

## **2 EXPERIMENTAL SECTION**

### **2.1 Preparation of FBE coatings and free standing films**

Five commercial FBE grades were selected among the most widely used for industrial applications as primers for 3LPO systems in the past two decades. A sixth grade of FBE was considered, this latter being suitable for use as 3LPO primer or monolayer anticorrosion coating. They are referred with letters from A to F.

FBE coated panels (150µm Dry Film Thickness specified) were prepared in the same industrial laboratory to minimise the differences during the preparation stage. FBE powders were spray applied on 50×100×3 mm<sup>3</sup> steel panels which were freshly grit-blasted to SA2 ½ according to ISO 8501 (R<sub>z</sub>=70µm). Cure cycles were performed according to each data sheet recommendation and polymerisation was checked by DSC (differences in T<sub>g</sub> between first and second run lower than 5°C). T<sub>g</sub> values were also measured at IFP on coatings as received as well as DFT (5 measurements for each coated face).

Free standing films (500µm DFT specified) were prepared by their respective manufacturers to ensure the best cure and post-cure conditioning. Panels (50 × 50 mm<sup>2</sup>) were cut out of films as received for testing purpose. DFT was measured on each panel prior to testing.

### **2.2 Preparation of three and bi-layer coating systems on tubes**

The steel preparation and coating application by longitudinal extrusion were performed in a plant according to TOTAL GSGRCOR220 and NFA49-710 on 8 steel pipes (0.114 m diameter and 12 m long) preheated to 220°C. Two pipes were coated with FBE material B with 80 µm and 250 µm nominal thicknesses and over-coated by adhesive material to reach an overall thickness around 500 µm. Two other pipes were coated with complete 3LPO systems (using MD type PE) including 80 µm and 250 µm of FBE B primer. Four other pipes were coated the same way using FBE primer F. Coated pipes were cut into short rings (0.25 m long) for the purpose of IFP study. Coating thickness values were checked on each ring as received. Bi-layer and three-layer coatings are called, respectively, 2L and 3L in the paper.

### 2.3 Testing of the FBE coatings and free standing films

**Adhesion.** Adhesion on low carbon steel was evaluated at room temperature by the cross-hatched test method (ISO 2409) before and during ageing. For ageing at 60°C, tests were performed on coatings freshly taken out of the water and cooled to room temperature. The disbonding was quantified by the percent of disbonded squares (adhesive rupture) relative to the total amount of squares intended with a knife to the metal.

**Differential Scanning Calorimetry.** DSC scan were carried out from -40°C to 250°C at 10°C/min on 10 mg specimen with a Q100 apparatus from Waters™. Commercial sealed specific pressured cells (upper pressure limit = 30 bar) were used to avoid the water desorption during heating. Dry T<sub>g</sub> was measured at the inflection on the heat flow curves obtained during the first run and second run (NFA 49-710). For soaked specimen, DSC measurements were performed on samples freshly taken out of the ageing medium and "wet T<sub>g</sub>" was measured at the inflection on the heat flow curve obtained during the first run. The lowering in T<sub>g</sub> can be calculated using following equation:

$$\Delta T_g = T_{g \text{ wet}} - T_{g \text{ dry}} \quad (\text{equation 2})$$

where T<sub>g wet</sub> and T<sub>g dry</sub> refer to the T<sub>g</sub> values measured in the first run for dry and wet states.

**Gravimetry.** One coating and two film panels per formulation were immersed in deionised water at two temperatures (20°C and 60°C) during 3 months. Samples were periodically removed from the solution, blotted dry and weighed to 0.1 mg with a Mettler AE 163. The water content in weight percent, M, was measured as the mass change with respect to the initial mass of the dry film.

### 2.4 Testing of the 2L and 3L coating systems on tubes

**Ageing.** 3L coated rings were aged in NaCl 1% at 20°C and 60 °C: the first series of tests was performed on complete coatings, the second series was performed on coatings with artificial defects (2 circumferential scarifications to the steel, 2 mm large and distant of 20 mm) and submitted to cathodic protection by potentiostatic polarisation (-1,5 V vs. Ag/AgCl). Graphite counter electrodes were placed in a separate cell filled with sodium sulphate and isolated by a cationic membrane to avoid any anodic dichloride formation by chloride oxidation. pH adjustment with HCl were conducted regularly to maintain pH values between 8 and 10.

2L coated rings were aged at 20°C and 60 °C by immersion in deionised water to simulate the electrolyte filtered by the thick PE top-coat acting as permselective membrane, where water molecules are supposed to diffuse much faster than ionic species [16].

**Peel test.** 2L and 3L coating peel strengths were measured on pipe rings at ambient atmosphere on a tensile machine at constant peeling velocity of 8.33x10<sup>-5</sup> m.s<sup>-1</sup> (5 mm.min<sup>-1</sup>). Mean strength values were calculated from the peeling data collected over almost the all circumference. The average peeling force expressed in N/m was also calculated in each case by dividing the mean peeling strength by the band width. The failure mode was recorded in each case following ISO 4624 criteria: A/B refers to an adhesive rupture between polymer and metal, B refers to a cohesive rupture within a given polymeric layer.

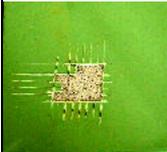
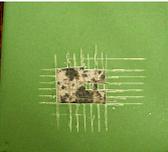
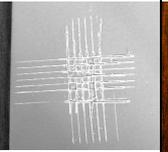
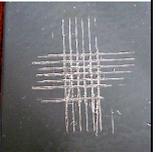
### 3 RESULTS

#### 3.1 Ageing of FBE coated and film panels

Adhesion to steel and physico-chemical properties ( $T_g$ ) were evaluated on coatings after 7 days and 90 days aging in hot water and compared to initial values in the dry state. The short term sampling corresponds to the FBE materials in the plasticized state due to reversible water diffusion/solubilisation within epoxies (according to gravimetric data the fickian plateau or pseudo plateau were reached after 7 days for all coatings). The long term sampling corresponds to FBE materials in the aged state - irreversible damage have possibly occurred.

**Adhesion of FBE coatings.** Results are reported in Table 1. Tests performed at 20°C on dry FBE materials reveals no disbonding, pointing out that there is no adhesive rupture in the dry state whatever the nature of FBE. Adhesion measured at 20°C after 7 days ageing points out a significant loss of adhesion for A and B FBE materials, where rupture became almost adhesive, whereas others keep their fully non adhesive failure mode. After 90 days ageing, FBE materials A and B still exhibit an almost full adhesive failure mode, as expected. Only FBE materials C and F keep an intact non adhesive failure mode whereas FBE D and E have a mixed rupture mode including partly adhesive disbonding.

**Table 1 - Adhesion loss measured by cross-hatched tests in dry and soaked states (% disbonded area)**

FBE coating	A	B	C	D	E	F
Dry state	0	0	0	0	0	0
7 days 60 °C	100	80	0	0	0	0
90 days 60°C	90	93	0	23	75	0
						

**$T_g$  measurements.**  $T_g$  values measured on coatings as received (Table 2) are quite similar whatever the FBE material – with somewhat increasing values between first and second run pointing out that infinite cure was not totally achieved. Wet  $T_g$  values measured on coatings after 7 days immersion at 60°C (plasticized state) and after 90 days immersion at 60°C (aged state) are also given in Table 2, as well as the shifts in  $T_g$  from dry to plasticized state and from dry to aged state calculated using equation 2. One can observe that wet  $T_g$  values are significantly lower than dry values, whatever the FBE, which stresses that the upper temperature limit must be defined according to the determination of wet  $T_g$  values to have the maximum operating temperature sufficiently lower than the wet  $T_g$  values and keep FBE coating materials in the glassy state during operating conditions (see § 1.3).

The comparison between plasticized and aged states show almost unchanged wet  $T_g$  values, suggesting that damage occurring during long term ageing (if any) are localized and do not affect the overall chain mobility. In terms of  $T_g$  lowering, aged FBE B coating exhibits the highest shift (around -30°C) whereas FBE F exhibits the lowest one

(around  $-15^{\circ}\text{C}$ ), revealing that B and F materials, respectively, are the more plasticized and the less plasticized by water. These observations can be correlated to the respective extreme adhesion behaviours of B and F coatings, as stated previously. However, wet  $T_g$  values and degree of plasticization cannot directly explain all the differences observed in the long term adhesion behaviours, e.g. FBE E and F have similar dry and wet  $T_g$  values but very differing long term adhesion behaviours. Thus, the inspection of other FBE properties is necessary to account for the long term adhesion behaviours.

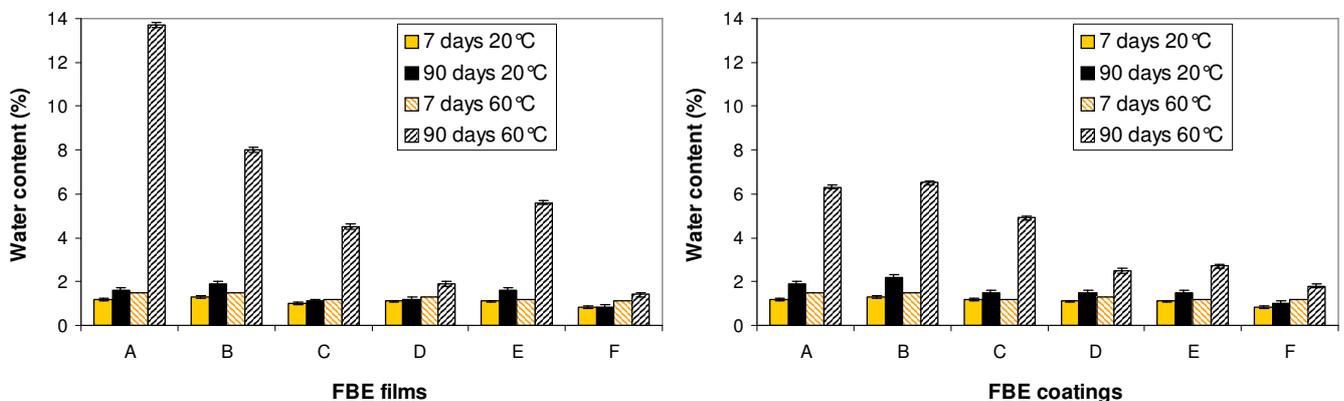
**Table 2 - DSC measurements of dry and wet  $T_g$  values ( $^{\circ}\text{C}$ ) and related  $\Delta T_g$**

FBE coating	A	B	C	D	E	F
Dry $T_g$ ( $^{\circ}\text{C}$ ) - 1 <sup>st</sup> run	103.2	105.9	101.5	102.6	101.8	101.3
Dry $T_g$ ( $^{\circ}\text{C}$ ) - 2 <sup>nd</sup> run	107.2	110.7	106.7	108.9	108.2	109.4
Wet $T_g$ ( $^{\circ}\text{C}$ ) - 7 days $60^{\circ}\text{C}$	82.1	80.7	84.4	84.1	83.0	84.4
Wet $T_g$ ( $^{\circ}\text{C}$ ) - 90 days $60^{\circ}\text{C}$	81.5	76.6	84.3	85.5	86.0	87.1
$T_{g \text{ wet 7days}} - T_{g \text{ dry 1st run}}$	-21.1	-25.2	-17.1	-18.5	-18.8	-16.9
$T_{g \text{ wet 90days}} - T_{g \text{ dry 1st run}}$	-21.7	-29.3	-17.2	-17.1	-15.8	-14.2

**Gravimetry.** Among numerous data collected during ageing and possible drawings, it was decided to present the water content (in weight %) measured after 7 and 90 days ageing at  $20^{\circ}\text{C}$  and  $60^{\circ}\text{C}$  for films and coated panels (Figure 1). Data are reported in Table 3 for free films and in Table 4 for coatings. From the comparison of water contents at 7 and 90 days at a given temperature, whatever coated or free film panel, it appears that there are two kinds of water uptake behaviours:

- (i) a classical fickian behaviour if the water content reaches a saturation level after one week immersion, corresponding to  $M_{7\text{days}}$  almost equal to  $M_{90\text{days}}$ ;
- (ii) an 'abnormal' behaviour for other cases when the water content steadily increases with time; then the water content at 7 days is taken as fickian pseudo-plateau.

According to these definitions, C, D, and F FBE materials exhibit a fickian behaviour at  $20^{\circ}\text{C}$  whereas only FBE F keeps a fickian behaviour at  $60^{\circ}\text{C}$ .



**Figure 1 - Water content (wt. % ) measured in FBE films (left) and coatings (right) during ageing in deionised water after 7 days and 90 days at  $20^{\circ}\text{C}$  and  $60^{\circ}\text{C}$**

**Table 3 - Water content (wgt. % ) measured in free films and coefficients of diffusion according to Fick law.**

FBE film	20°C			60°C		
	M <sub>7 days</sub> (%)	M <sub>90 days</sub> (%)	D (m <sup>2</sup> /s)	M <sub>7 days</sub> (%)	M <sub>90 days</sub> (%)	D (m <sup>2</sup> /s)
A	1,20 ±0,05	1,60 ±0,10	1,8 ±0,2.10 <sup>-13</sup>	1,5 ±0,05	13,7 ±0,10	10±2.10 <sup>-13</sup>
B	1,30 ±0,05	1,90 ±0,10	1,8 ±0,2.10 <sup>-13</sup>	1,5 ±0,05	8,0 ±0,10	10±2.10 <sup>-13</sup>
C	1,00 ±0,05	1,10 ±0,10	1,6 ±0,2.10 <sup>-13</sup>	1,2 ±0,05	4,5 ±0,10	15±2.10 <sup>-13</sup>
D	1,10 ±0,05	1,20 ±0,10	1,5 ±0,2.10 <sup>-13</sup>	1,3 ±0,05	1,9 ±0,10	14±2.10 <sup>-13</sup>
E	1,10 ±0,05	1,60 ±0,10	2,0 ±0,2.10 <sup>-13</sup>	1,2 ±0,05	5,6 ±0,10	12±2.10 <sup>-13</sup>
F	0,85 ±0,05	0,85 ±0,10	2,5 ±0,2.10 <sup>-13</sup>	1,1 ±0,05	1,4 ±0,10	15±2.10 <sup>-13</sup>

**Table 4 - Water content (wgt. % ) measured in coatings and coefficients of diffusion according to Fick law.**

FBE coating	20 °C			60 °C		
	M <sub>7 days</sub> (%)	M <sub>90 days</sub> (%)	D (m <sup>2</sup> /s)	M <sub>7 days</sub> (%)	M <sub>90 days</sub> (%)	D (m <sup>2</sup> /s)
A	1,20 ±0,05	1,9 ±0,10	1,0 ±0,2.10 <sup>-13</sup>	1,5 ±0,05	6,3 ±0,10	6 ±2.10 <sup>-13</sup>
B	1,30 ±0,05	2,2 ±0,10	1,0 ±0,2.10 <sup>-13</sup>	1,5 ±0,05	6,5 ±0,10	4 ±2.10 <sup>-13</sup>
C	1,20 ±0,05	1,5 ±0,10	0,6 ±0,2.10 <sup>-13</sup>	1,2 ±0,05	4,9 ±0,10	7 ±2.10 <sup>-13</sup>
D	1,10 ±0,05	1,5 ±0,10	1,5 ±0,2.10 <sup>-13</sup>	1,3 ±0,05	2,5 ±0,10	5 ±2.10 <sup>-13</sup>
E	1,10 ±0,05	1,5 ±0,10	1,7 ±0,2.10 <sup>-13</sup>	1,2 ±0,05	2,7 ±0,10	8 ±2.10 <sup>-13</sup>
F	0,85 ±0,05	1,0 ±0,10	1,0 ±0,2.10 <sup>-13</sup>	1,2 ±0,05	1,8 ±0,10	6 ±2.10 <sup>-13</sup>

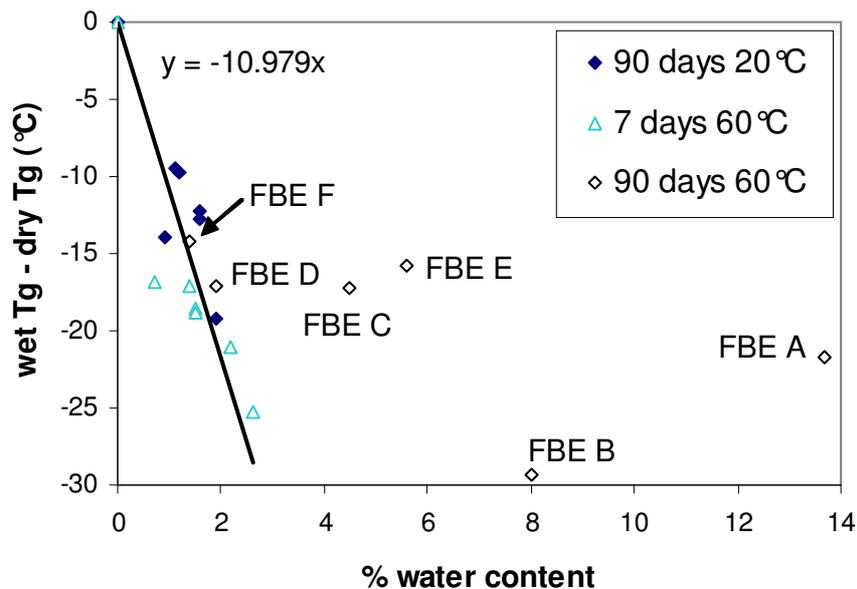
The analysis of the short term behaviour of FBE materials leads to following remarks:

- The water uptake curves can be modelled in the short term stage using the Fick's law with the water content at 7 days as (apparent) saturation value. Diffusion coefficients reported in Table 3 for free films and Table 4 for coatings are in very close agreement at a given temperature for each FBE. Thus, from a practical point of view, gravimetry data collected on coated materials can be interestingly used to study the water uptake behaviour of the FBE material if no free standing films are available.
- The water contents measured after 7 days are almost independent of the temperature but vary significantly with the FBE material, confirming that the FBE nature governs the water solubility in the plasticized state. The less hydrophilic material is the FBE F whereas FBE B appears as the most hydrophilic. These results support the previous conclusion on the degree of plasticization by water.

The analysis of the long term behaviour of FBE materials leads to following remarks:

- The non stabilized water uptake curves could be satisfactorily modelled using Langmuir or Berens and Hopfenberg approaches, adapted from the Fickian model.
- The water contents measured after 90 days are very depending on the FBE material and, more precisely, on its durability at the ageing temperature; water contents after 3 months immersion at 20°C remain below 2% whereas results are very dispersed at 60°C, with high values for A and B FBE materials. These results suggest that those later may be particularly sensitive to hydrolysis in hot water due to their chemical nature.

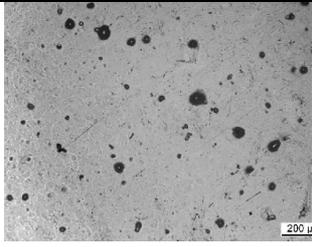
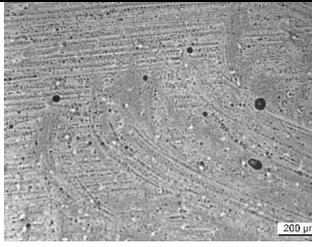
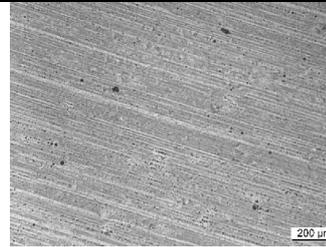
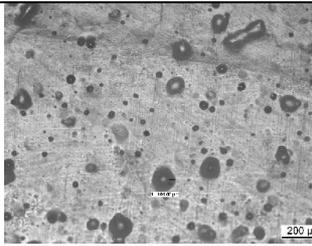
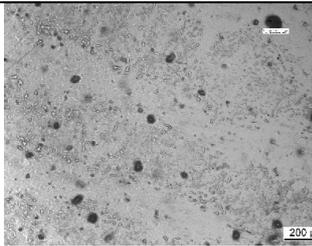
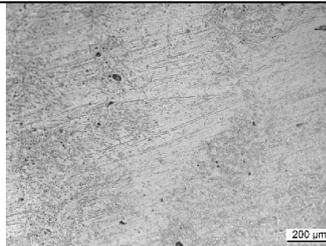
Additional understanding can be achieved when plotting  $\Delta T_g$  in function of the water content for the six FBE materials (Figure 2). As main trend, one can observe that the  $T_g$  is shifted proportional to the water content (-11 degrees per wgt. percent) when pure plasticization by water occurs, as reported in the literature [17, 18]. But some points escape from this trend revealing possible osmotic degradation (water content increases whereas wet  $T_g$  remains stable) or advanced network hydrolysis ( $T_g$  decreases whereas water content remains stable or even diminishes due to small mass loss).



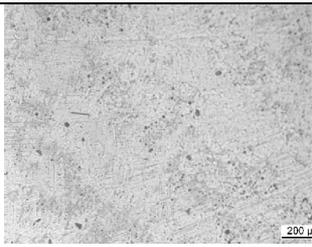
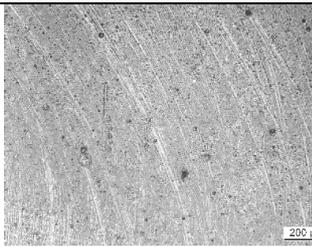
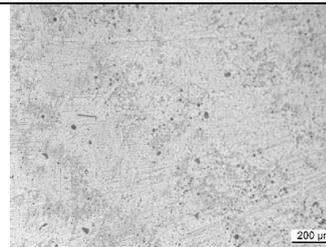
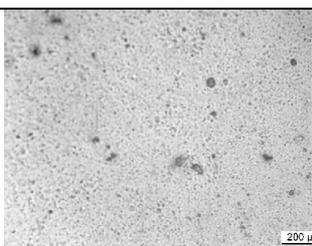
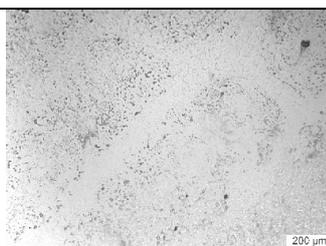
**Figure 2 - Delta  $T_g$  versus water content for the 6 FBE materials during ageing.**

**Evidence of osmotic degradation.** Optical microscopy observations ( $\times 200$ ) were performed on dry and aged films to characterise the possible development of blistering due to osmotic degradation which often accompanies polymer hydrolysis [19]. Pictures given in Table 5 clearly point out the presence of porosities with diameters larger than  $10\mu\text{m}$  after ageing for FBE A ( $\sim 70$  porosities/ $\text{cm}^2$ ) and B ( $\sim 20$  porosities/ $\text{cm}^2$ ). Osmotic degradation may also have started in FBE D. Blisters within FBE material and related ones developed at the coating/metal interface will obviously affect the long term adhesion to steel for FBE materials A, B and D.

**Table 5 - Photographs of FBE films in dry and aged states given by optical microscopy ( $\times 200$ ).**

FBE film	A	B	C
Dry state			
90 days 60°C			

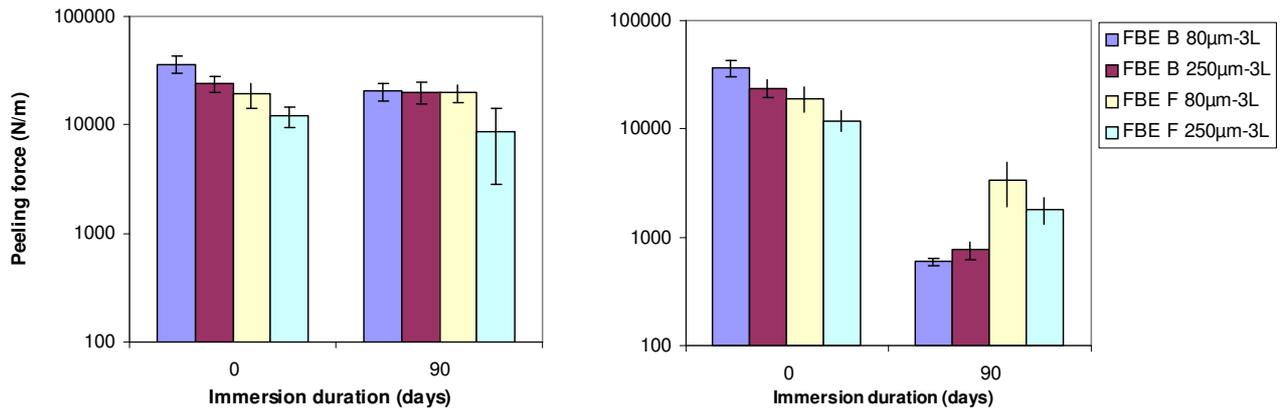
FBE film	D	E	F
Dry state			
90 days 60°C			

For the second part of the study, two epoxy powders were selected for their differing behaviours in terms of water content and durability while exposed to deionised water at 60°C:

- FBE B: very hydrophilic material and sensitive to osmotic blistering,
- FBE F: with little water uptake and a stable behaviour after three months exposition.

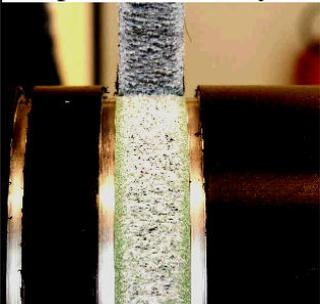
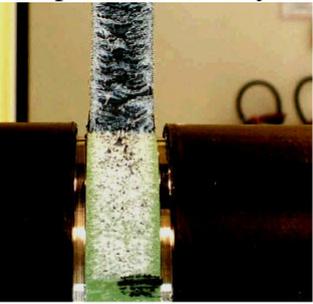
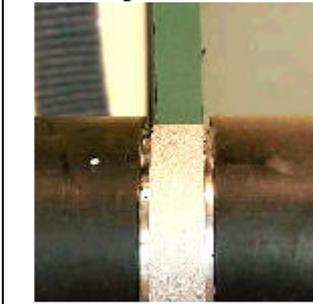
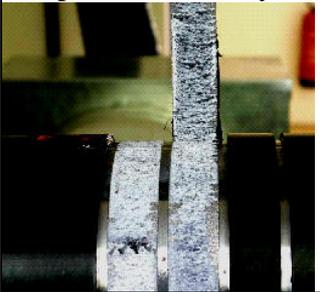
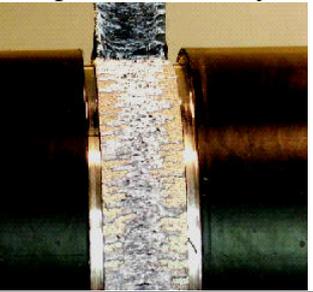
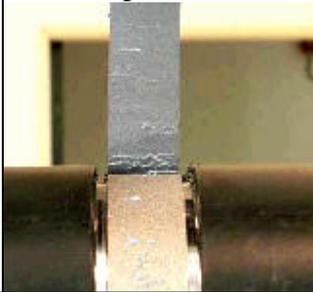
### 3.2 Ageing of coating systems

Main results of peeling tests performed on complete 3L coatings (no artificial defect) are presented before and after ageing in Figure 3 and illustrated in Table 6. It can be pointed out that adhesion is almost unchanged after 3 months immersion at 20°C and ruptures remain cohesive within tie layer. On the contrary, there is a significant loss of adhesion after 3 months immersion at 60°C and ruptures become adhesive, whatever the FBE. Interestingly, the loss of adhesion is clearly stronger for systems based on powder B, which may be directly related to their higher water content in the plasticized state. Note that there is no corrosion found below the 3L coatings under consideration, only white metal.

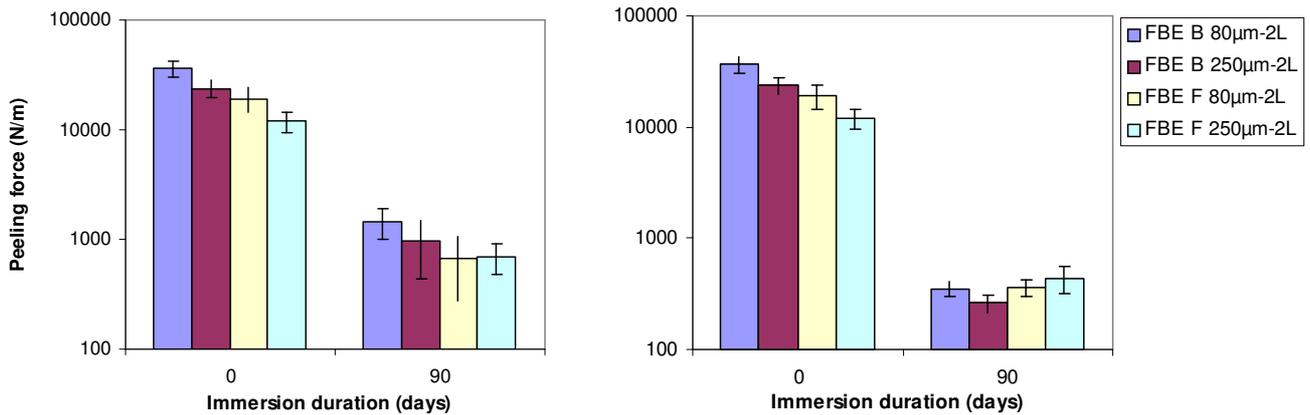


**Figure 3 - Peeling force of 3L coatings aged in NaCl 1% at 20°C (left); 60°C (right)**

**Table 6 - Photographs of peeled areas for 3L coatings before and after 3 months ageing in NaCl 1% at 20°C and 60°C.**

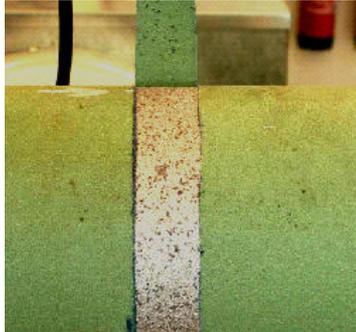
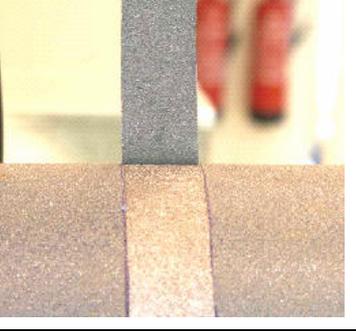
3L coatings	Before ageing	90 days ageing 20°C	90 days ageing 60°C
FBE B 80µm	728 ± 125N rupture B in tie layer 	410 ± 75N rupture B in tie layer 	12 ± 1N rupture A/B 
FBE F 80µm	384 ± 96N rupture B in tie layer 	398 ± 73N rupture B in tie layer 	68 ± 30N rupture A/B 

Main results of peeling tests performed on complete 2L coatings (no artificial defect) are presented before and after ageing in Figure 4 and illustrated in Table 7. There is a significant loss of adhesion after 3 months ageing at 20°C for both powders, however only FBE B exhibits an adhesive failure. The loss of adhesion is greater after ageing at 60°C and adhesive failure are observed in any cases. Besides, numerous corrosion points can be observed under FBE B aged at 60°C whereas metal underneath FBE F is just slightly grey. Thus interfacial corrosion seems prone to develop under powder B. It may be concluded that blisters which are likely to develop within FBE B after 3 months ageing at 60°C could act as preferential areas for the initiation of corrosion [20].



**Figure 4 - Peeling force of 2L coatings aged in deionised water at 20°C (left); 60°C (right).**

**Table 7 - Photographs of peeled areas for 2L coatings before and after 3 months ageing in deionised water at 20°C and 60°C.**

2L coatings	Before ageing	90 days ageing 20°C	90 days ageing 60°C
FBE B 80µm	Impossible	28 ± 9N rupture A/B 	7 ± 1N rupture A/B 
FBE F 80µm	Impossible	13 ± 8N rupture B in FBE 	7 ± 1N rupture A/B 

From abovementioned results on 3L and 2L systems, major trends highlighted by the peel tests within 3 months are the massive adhesion loss due to water entrance and the cohesive rupture becoming adhesive. The higher disbonded rate noted in 3L systems with powder B may be related to the faster development of corrosion under 2L coatings with powder B. Thus testing on 2L system used for accelerating the water ingress through a 3L undefectuous system is also validated for accelerating the hydrolysis attack and the corrosion development.

## 4 CONCLUSIONS

The long term adhesion of FBE is a critical functionality required from 3LPO coatings along the pipe lifetime but water permeability through a 3LPO system without defect cannot be neglected. Thus focus was made on the FBE behaviour in a wet environment. A comparative study was launched by TOTAL to link the wet behaviours of commercial FBE materials to the long term adhesion to steel of complete 3LPO systems which were plant applied on tubes to represent undefectuous industrial coatings. The peeling results obtained on complete 3L systems on tubes pointed out substantial losses of adhesion after three months immersion, even at 20°C since the peel strengths were almost divided by two. Peel tests on complete 3L and 2L coatings showed that systems with powder B are more sensitive to wet ageing than systems with powder F since loss of adhesion was higher in 3L-FBE B systems and metal corrosion occurs faster under 2L-FBE B systems. These results could be related to the intrinsic properties of FBE as standalone coatings and films ; in particular powder B was shown to be highly hydrophilic and sensitive to hydrolysis in hot water. Then it was concluded that the blisters which developed within FBE B after 3 months ageing at 60°C could act as preferential areas for the initiation of corrosion in 3LPO systems.

From the work, it was also concluded that two criteria must be considered for a proper selection of FBE powders, given a maximum operating temperature, to ensure the long term adhesion in service conditions:

- the wet Tg must be higher than max operating temperature to operate FBE material in the glassy state and keep proper mechanical properties (good adhesion) and electrical properties (good barrier); mind that the wet Tg is always inferior to the dry Tg due to FBE plasticization by water uptake, in some cases a fifty degrees lowering can be observed;
- the durability in water at the maximum operating temperature must be good; a poor resistance to hydrolysis will undoubtedly affect the mechanical anchoring to steel but may also lead to osmotic blistering which can act as corrosion promoter on steel.

The next step will be to study coated tubes taken out from production pipes operating in various places.

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