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USE OF EIS FOR THE MONITORING AND MODELLING OF MULTI-LAYER ANTICORROSION COATINGS

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Abstract

Three-layer polyolefin coatings are being used classically for external pipeline protection in the oil and gas industries over years although cathodic protection is also applied. They 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, the permeability of polyolefin top-coat to water is not negligible and thus does not prevent water ingress into sub-layers after a few months service. Then soaked water in the vicinity to the steel pipe conveying hot effluents possibly induces hydrolysis of the epoxy primer layer and interfacial bonds to metal. This could raise questions over the long term corrosion control. Therefore, the inspection of the water ingress and the investigation of the long-term barrier properties of primer and adhesives layers when exposed to water are mandatory.

This paper examines the use of Electrochemical Impedance Spectroscopy (EIS) to monitor durability and anticorrosion properties of three-layer coatings while exposed to water at 60 °C (maximum service temperature). The objective was to investigate the water ingress within a bilayer coating with respect to sublayer thickness. EIS was used to characterise the water uptake but also the long term barrier properties of coatings on industrial tubes. In complement, gravimetry measurements were also performed during ageing on FBE primer coated panels cut from industrially coated tubes to determine the water uptake kinetics using classical destructive techniques. Degradation mechanisms of 3LPO and potentiality of EIS technique are discussed in the paper.

Keywords : organic coatings, multi-layer, water uptake, polymer degradation

1. Introduction

Three-layer polyolefin coatings (3LPO) are being used classically for external pipeline protection in the oil and gas industries over years although cathodic protection is also applied. Such coatings consist of typically an epoxy primer layer (Fusion Bonded Epoxy) providing both adhesion and corrosion protection to steel, overlaid by an intermediate adhesive layer ensuring the proper anchoring of the polyolefin top-coat to the epoxy primer. The use of an external polyolefin top-coat (polyethylen or polypropylen) 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).

Recent case studies reported large scale disbondments of 3-LPO coatings, which could favour corrosion beneath the pipe coating and lead to possible leakage or other major damage (1-4). Indeed, polyolefin materials are well known for their very tiny water uptake while exposed to vapor or liquid water but their permeability to water is not negligible (5). Thus polyolefin top-coats do not prevent water ingress into sub-layers after a few months service and soaked water in the vicinity to the steel pipe conveying hot effluents possibly induces hydrolysis of the epoxy primer layer and interfacial bonds to metal which, in turn, could raise questions over the long term corrosion control (6,7). This is particularly critical for 3LPO coatings since they are prone to 'shielding effect': when water flows along the metal surface under a disbonded 3LPO, cathodic protection current is likely to be unable to reach the pipe because of the high dielectric strength of polyolefin.

Therefore, the inspection of the water ingress and the investigation of the long-term barrier properties of primer and adhesives layers when exposed to water are mandatory. IFP started to work in this thematic three years ago and proposed a methodology based on the ageing of bi-layer FBE/adhesive coatings as stand alone systems to provide an accelerated measurement of the FBE adhesion to steel during wet ageing (8,9): peel tests are carried out on pipe rings industrially coated with FBE and adhesive to examine the adhesion of sub-layers to steel under wet exposure and directly investigate the effect of water permeation through the coating. This cannot be achieved while submitting 3LPO systems to cathodic disbonding tests since the influence on adhesion performance of FBE wet ageing due to water diffusion through the coating cannot be distinguished from ageing related to cathodic disbonding mechanisms and water entrance in intended defect (10,11).

In addition to a better understanding of failure mechanisms and to the development of new hydrophobic epoxy primers for 3LPO coatings (12), there is a need of non destructive methodologies to allow the health monitoring of the coating. The objective of this study was to investigate the potentials of EIS for the monitoring of 3LPO anticorrosion coating. For that purpose, pipe rings coated with the FBE primer layer only were studied as well as bilayer coated pipe rings. EIS characterisation of FBE and FBE/adhesive coatings exposed to water at 60°C are presented in the result part. The influence of the layer thickness is discussed.

2 Experimental

2.1 Coating composition and application

Materials were selected among those currently used for industrial applications. The steel preparation and coating application were performed in a plant according to GDF specification SPEC PC Rv 06 on 4 steel pipes (0.11 m diameter and 6 m long).

Two pipes were coated with FBE material (initial Tg = 105°C measured by DSC according to NF A- 49710) for two specified mean thickness: 100 µm and 300 µm. Two other pipes were coated with same FBE primers and over-coated by adhesive material to reach an overall specified thickness around 500 µm. Then coated pipes were cut into short rings (0.3 m long) for the purpose of IFP study.

Systems with, respectively, 100 µm and 300 µm FBE thickness are referred to "B" and "C" in this paper. Coating thickness values checked on each ring as received are presented in Table 1. The adhesive thickness was estimated from bilayer and monolayer thickness values.

Table 1 - Thickness in microns (mean values & standard deviation) of coating layers

Thickness (µm)	B	C
FBE primer layer	94 ± 24	300 ± 34
Adhesive layer	351 ± 53	200 ± 63

2.2 Ageing conditions

Coatings as received were aged in deionised water at 60°C on rings. The electrolyte was preferably chosen with high ionic purity to simulate the filtered water by the PE top-coat. Indeed, the polyolefin is supposed to work as a perm-selective membrane, i.e. only the molecules such as water, oxygen, carbon dioxide diffuse but ionic species remain in the external medium. However, continuous water uptake monitoring by EIS on coated pipe rings was performed in 1 % NaCl aqueous solution to ensure sensible impedance measurements.

Small size panels cut into the pipe rings were also used for a classical gravimetric study of water uptake. The rate of the water sorption was measured as the rate of mass change with respect to the initial mass of the dry FBE material (the steel was weighted at the end of sorption tests after burning of the organic material).

2.3 EIS tests

Impedance Spectroscopy measurements are carried out by means of a Solartron™ Frequency Response Analyzer FRA1260 equipped with a specific dielectric interface 1296 to measure large impedance values. The impedance data are obtained over a frequency range of 100 kHz to 100 mHz using a 100 mV amplitude of sinusoidal voltage. Simple two-electrode configurations electrode/material/electrode are used to characterize the impedance properties of coated rings exposed to a 1% NaCl aqueous solution during ageing (Figure 1). Measurements were performed in isothermal conditions at 60°C with exposed area of 3.1 cm^2 or 10.9 cm^2.

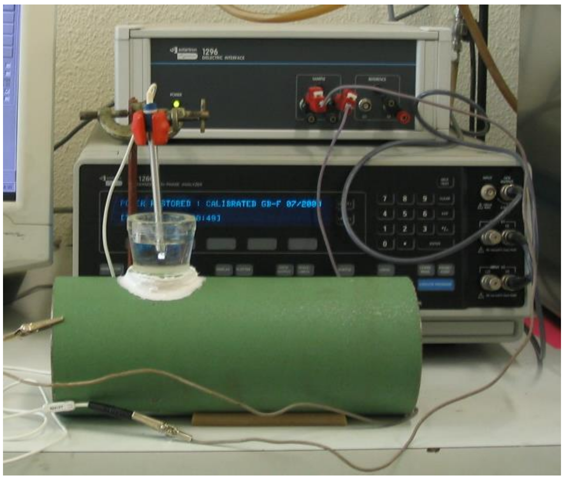


Figure 1 - Illustration of EIS characterisation of mono / bilayer coated pipe rings

2.3 Adhesion tests

Bi-layer coating peel strengths were measured on pipe rings at ambient atmosphere on a tensile machine at constant peeling velocity of 8.33×10^{-5} $m.s^{-1}$ (5 $mm.min^{-1}$). The polymer band cut to metal prior to the peel test was 20mm width. The peel energy in $J.m^{-2}$ is calculated by dividing the peel strength (N) by the band width (m).

FBE primer coating adhesion was evaluated by pull-off tests specified by ISO 4624 (measurements were performed using 3 dollies).

3 Results

3.1 Short term monitoring

EIS is a powerful tool to perform in situ and non destructive monitoring of the water uptake on organic coatings (13-15), provided relaxations due to the glass transition of the plasticized coating matrix do not occur in the temperature range of the measurement (16,17). This first part deals with the use of EIS to monitor water ingress in FBE primer. The water uptake of B-FBE coating at 60°C as revealed by the capacitance evolution versus the square root of time is displayed in Figure 2a.

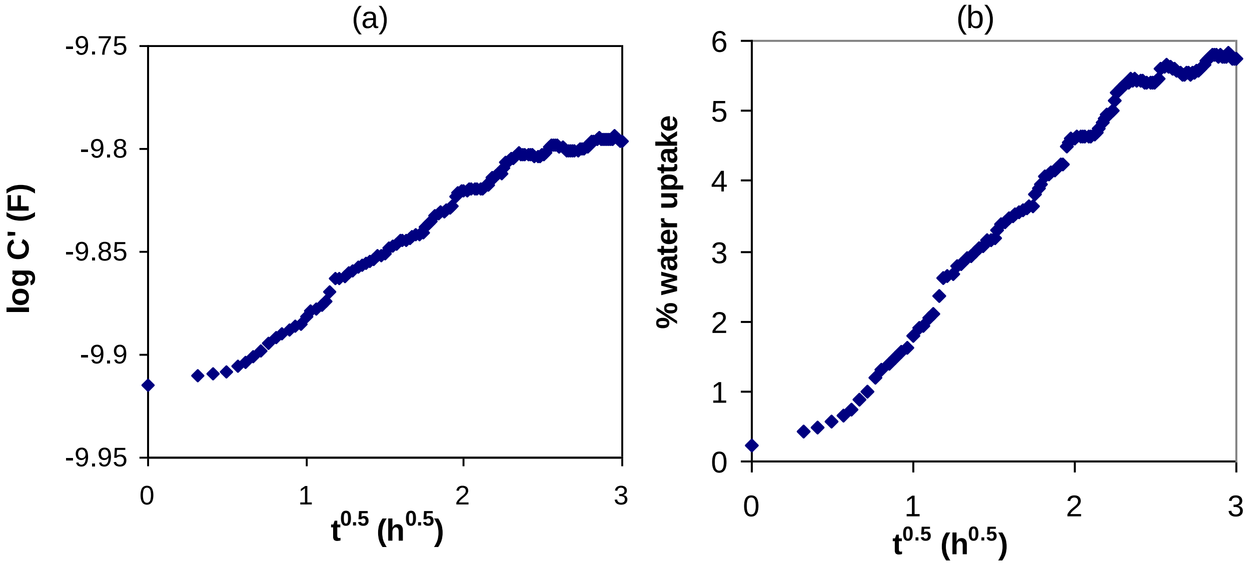


Figure 2 - Short term water uptake monitoring by EIS in the B-FBE coating at 60°C a) capacitance (10000Hz) evolution with square root of time; b) water content given by EIS according to Brasher and Kingsbury law (13).

From the capacitance values at 10000 Hz, the water content evolution was calculated using the Brasher and Kingsbury law (13).

$$\phi = \log (C_t/C_0)/[\rho \log(\varepsilon_w)] \quad \text{(equation 1)}$$

where ϕ stands for the mass gain given by EIS, C_t stands for the capacitance at t, C_0 stands for the capacitance at time 0 (dry film), ρ is the density of polymer film and ε_W is the permittivity of water ($\varepsilon_W = 63$ *at 60°C).*

In a second step, diffusion coefficient D was evaluated through equation 2 according to a Fickian behavior for the water absorption (18):

$$\frac{M_t}{M_\infty} = 1 - \left(\frac{8}{\pi^2}\right) \sum_{n=0}^{\infty} \left(\frac{1}{(2n+1)^2} \times \exp\left(-2(n+1)^2 \pi^2 \left(\frac{Dt}{l^2} \right) \right) \right) \qquad \text{(equation 2)}$$

where M_t is the mass of water absorbed at time t, M_∞ is the mass of water at infinite time t_∞ and l is the thickness of film.

Given the high water content estimated at saturation after 9 hours exposition (Figure 2b), we had some assumptions that the water content could be overestimated due to the plasticization of the glass transition. Thus, the water uptake at 60°C of a B-FBE coated panel was also studied by gravimetry to asses EIS results (Figure 3).

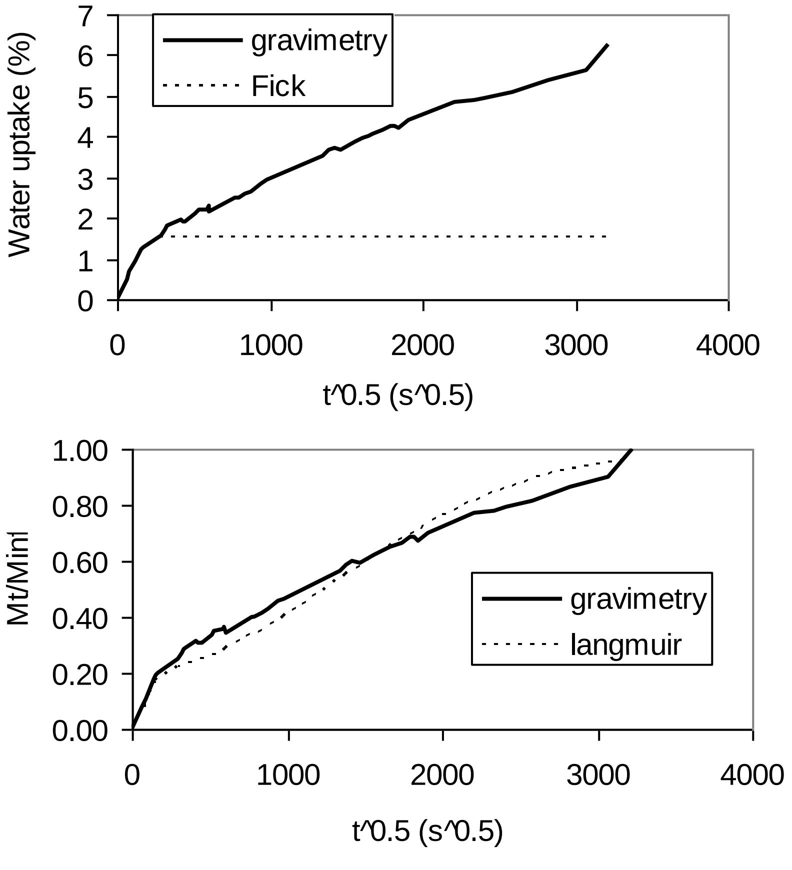


Figure 3: Water uptake behavior versus square root of time followed by gravimetry for the B-FBE coating immersed in deionised water at 60°C

a) experimental water content (in weight %) and fick modelling; b) reduced water content M_t / M_∞ and Langmuir modelling

In fact, the aforementioned overestimation is likely to occur since the water content after one week exposition is estimated around 1.5% by gravimetry - much lower value than EIS results. Since the long term gravimetric results on FBE coating exhibit a steadily increasing water content, sign of hydrolytic or osmotic degradation, trials were done to fit gravimetric data with the diffusion law of Langmuir (18), equation 3, which should give more appropriate results than the classical diffusion law of Fick :

$$\frac{M_t}{M_\infty} = 1 - \frac{\gamma}{\alpha+\gamma} e^{-\alpha t} - \frac{8}{\pi^2} \frac{\alpha}{\alpha+\gamma} e^{-\gamma t} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} e^{\frac{-D(2n+1)^2 \cdot \pi^2 \cdot t}{h^2}}$$

(equation 3)

where M_t is the mass of water absorbed at time t,

M_∞ is the mass of water at infinite time t∞,

l is the thickness of film,

α is the probability of water to be linked to the polymer,

γ is the probability of linked water to be released.

Model parameters obtained from in situ impedance and ex situ gravimetry results for B-FBE coating immersed in deionised water at 60°C are presented in Table 2.

Table 2 – Model parameters obtained by fitting experimental ex situ gravimetry and in situ impedance data of water uptake in B-FBE primer immersed in water at 60°C.

	Gravimetry	EIS
Fick water content at equilibrium (wt.%)	1.5	6.0
Fick diffusion coefficient (m^2/s)	6.0×10^{-13}	5.4×10^{-13}
Langmuir α (/s)	10^{-6}	-
Langmuir γ (/s)	0.333×10^{-6}	-

Diffusion coefficient and water content at equilibrium are obviously not in close agreement at 60°C for this FBE. Thus, the capacitance change measured at 60°C is not only directly related to the increasing material permittivity with water entrance. It is overlapped by the capacitance increase related to Tg lowering by FBE plasticization. In fact, this is not completely surprising since epoxy resins classically exhibit a lowering of 20°C per percent of water uptake (19). Given the initial Tg value and the water content reached within 9 hours (= 1.5 %), then the wet Tg value could be expected around 75°C, i.e. not sufficiently differing from the aging temperature to allow a quantitative use of Brasher law. As a consequence, the langmuir model will be useful to offer a more appropriate simulation of the water ingress into bi-layer coatings than the one proposed in previous works (8,9) on the basis of EIS data only.

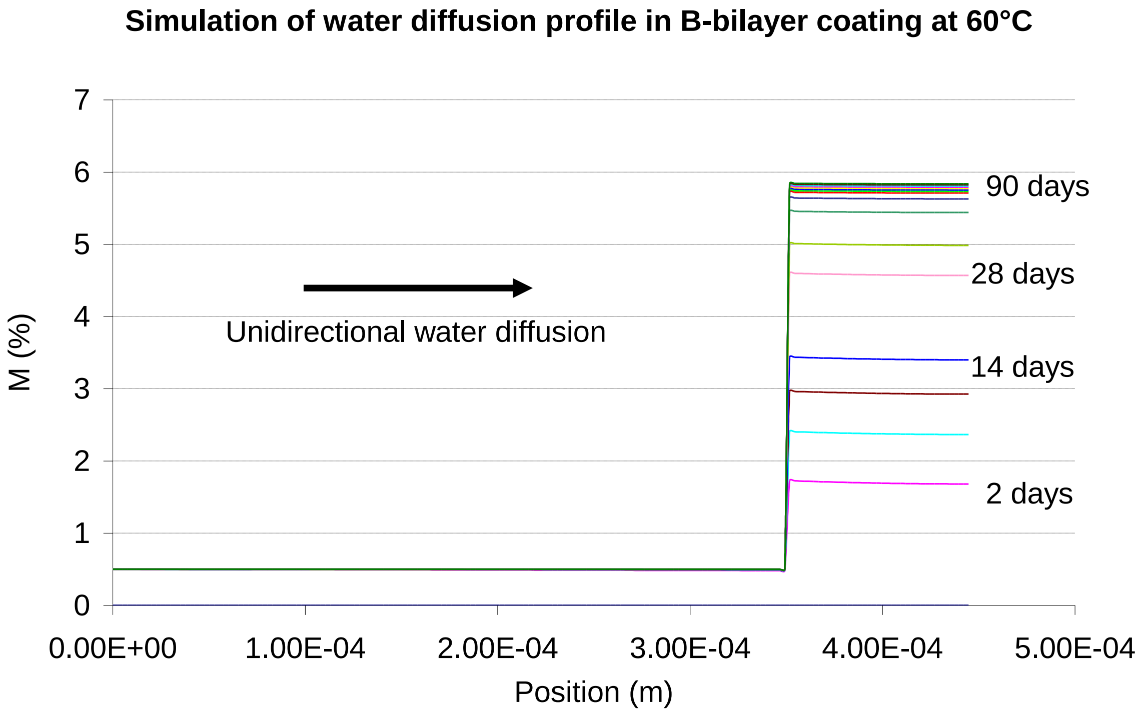
In conclusion, the use of EIS to quantitatively evaluate the water uptake kinetics in FBE materials having initial Tg values around 100°C should be limited to lower temperature range than 60°C. Nevertheless, as FBE formulations improve towards higher Tg values (12), future works to characterize their behavior in water should again investigate the potentiality of EIS.

3.2 Long term monitoring

In this part, the potentiality of EIS measurement to detect irreversible damage occurring in the coating material and/or at the metal surface was investigated. Unidirectional water ingress modelling was performed in B and C bi-layer coatings exposed to water at 60°C. As discussed previously, the Langmuir law to simulate the diffusion of water in the FBE primer layer whereas the Fick law was used to simulate the water diffusion through the adhesive layer, with the hypothesis of 0.4% of water content at saturation and a diffusion coefficient value of 4.10^{-12} m^2/s (8). Simulations given on Figure 4 show that a three months ageing period should be fully sufficient for systems under consideration to reach a high level of water content in the FBE near the metal surface and investigate the consequences on barrier properties.

B and C bi-layer coated rings were aged in deionised water at 60°C for a 3 months period. B-FBE and C-FBE coatings were also aged in similar conditions. Various coating properties (Table 3) were evaluated prior and after ageing:

- coating aspect (visual inspection),
- mechanical properties (adhesion measurement),
- water content (thermo-gravimetric analysis).


Simulation of water diffusion profile in B-bilayer coating at 60°C

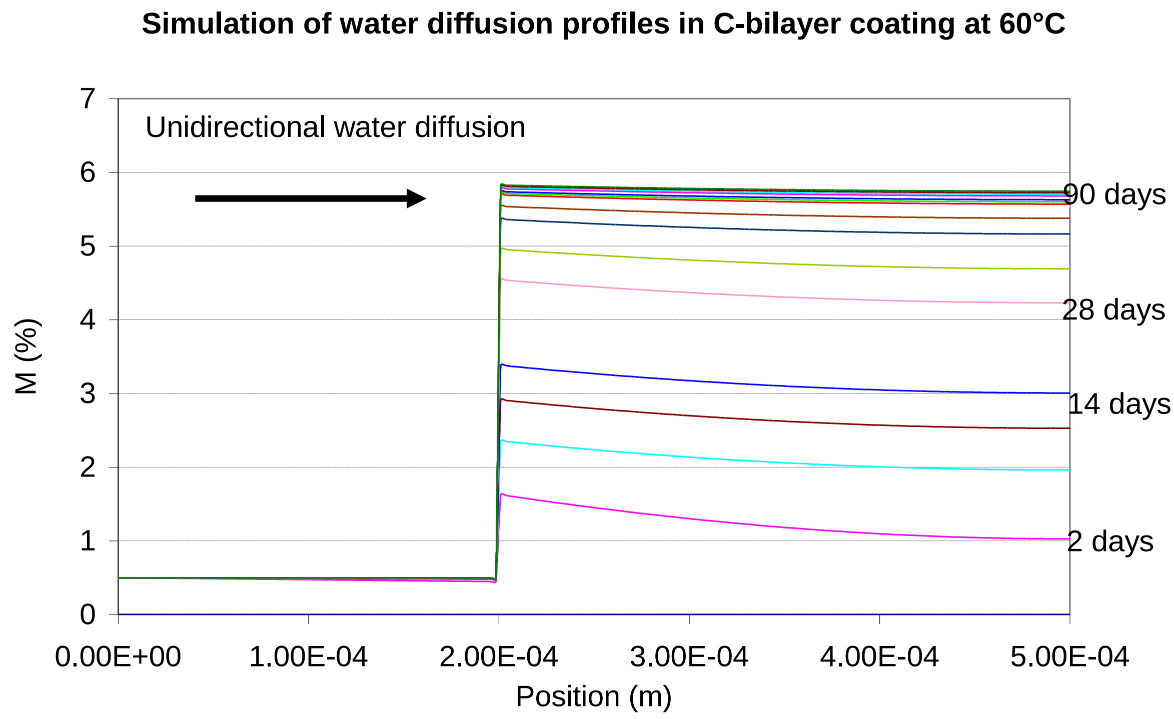

Simulation of water diffusion profiles in C-bilayer coating at 60°C

Figure 4 – Simulation of water concentration profiles in B-bilayer and C-bilayer coatings exposed to deionised water at 60°C – Hypothesis of unidirectional diffusion (fick law in adhesive layer / langmuir law in FBE layer)

Table 3 – Coating properties prior and after 3 months ageing in water at 60°C

System	Property	Initial state	After 3 months ageing in water at 60°C
B-FBE primer	Visual inspection	Smooth coating	Numerous blisters
	Adhesion (pull-off test)	18 ± 2 MPa glue rupture White metal	3 ± 0 MPa 100% adhesive rupture Black metal
	Water content (%)	0	2.0
C-FBE primer	Visual inspection	Smooth coating	Cracks to the metal
	Adhesion (pull-off test)	9 ± 1 MPa 100% cohesive rupture	5 ± 1 MPa 100% adhesive rupture Black metal
	Water content (%)	0	12.3
B-bilayer	Visual inspection	Rough coating	Rough coating
	Adhesion (peel test)	29 000J/m^{2} * White metal	250J/m^{2} Grey metal + metallic particles on peeled strip
	Water content (%)	0	1.6
C-bilayer	Visual inspection	Rough coating	Rough coating
	Adhesion (peel test)	29 000J/m^{2} * White metal	500J/m^{2} Grey metal
	Water content (%)	0	2.6

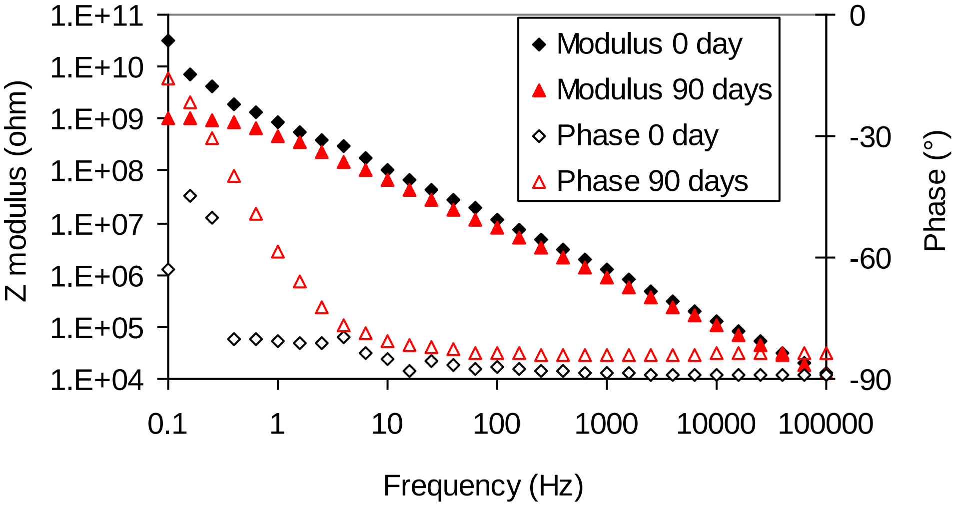
* Measured in fact on a 3LPO system (9)

EIS characterization was performed at 60°C at the beginning and at the end of the ageing time for all coatings under consideration. Results on FBE coatings are presented as Bode spectra on Figure 5. Curves before ageing exhibit an almost capacitive behaviour which is characteristic of an intact coating. Then the apparition of a resistance in both B and C aged FBE coatings means:

- the water plasticized the B-coating (see water content) and the Tg becomes closer to the temperature of the measurement, then the film resistance decreases; actually, tiny porosities in the blistered primer B would also lead to similar trends but, unfortunately, no EIS was performed with an electrolyte of higher conductivity to check the second hypothesis (17).

- a degradation of the C-FBE coating (cracks lower substantially the pore resistance) which dominates the effect of coating plasticization.

(a) B-FBE primer coating aged in water at 60°C



(b) C-FBE primer coating aged in water at 60°C

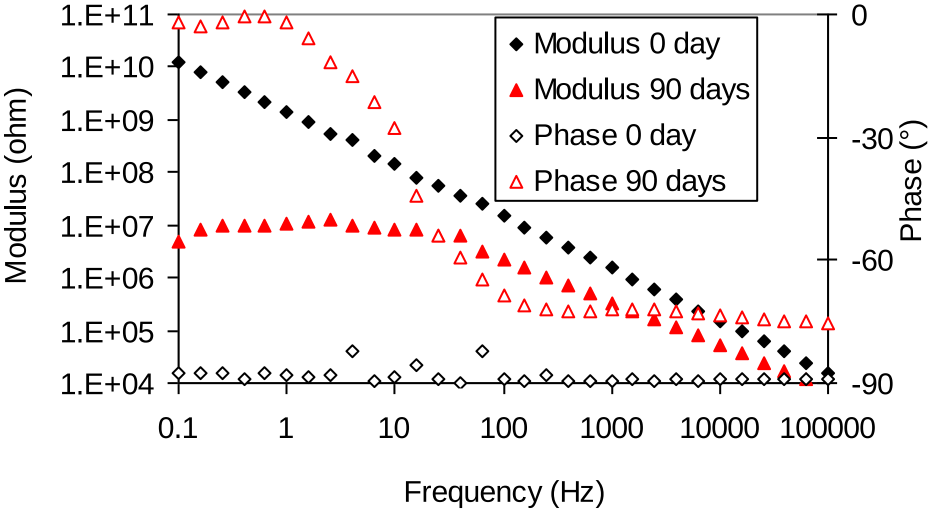
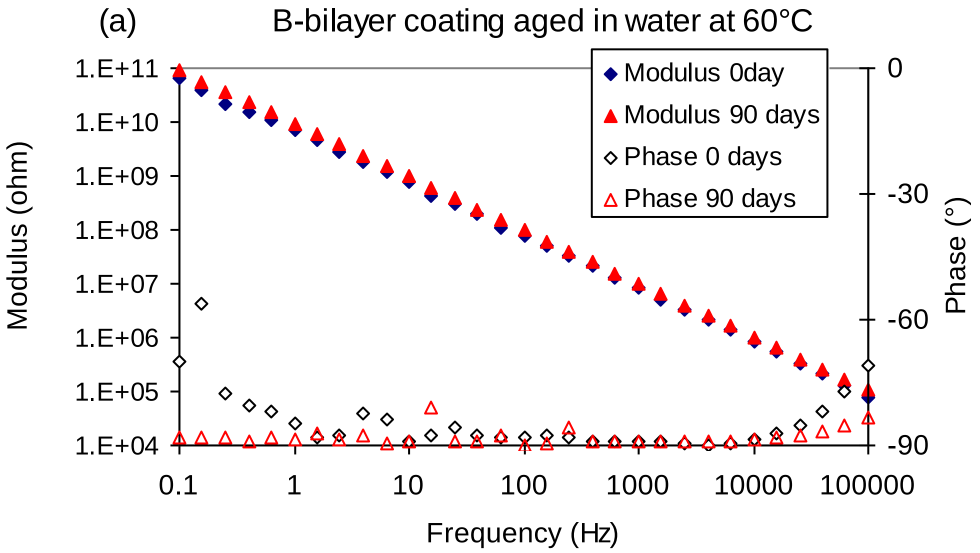


Figure 5 - Evolution with ageing time of the Bode plots for (a) B-FBE coating and (b) C-FBE coating exposed to deionised water at 60°C

EIS results on bilayer coatings are presented as Bode spectra on Figure 6. Both systems present differing behaviours:

- B-bilayer coating seems almost unchanged with ageing with respect to EIS behaviour, whereas other visual, mechanical and physico-chemical properties indicate that the coating material is plasticized and that magnetite (corrosion product) developed on the steel surface; the EIS response of the plasticized FBE (see phase increase in the low frequency range) is clearly dominated by the capacitive response of the adhesive layer acting as 'electrical shield'.

- C-bilayer coating after ageing exhibits a new relaxation on EIS spectra in intermediate frequency range; the formation of water clusters within the FBE / at metal surface while the adhesive layer remains an efficient electrical barrier (no ionic flow between electrolyte and steel surface) could explain this new relaxation. Besides, the high frequency capacitance is strongly diminished. This later could be attributed to thickness increase due to possible swelling and blistering in the primer, as observed in the stand alone B-coating. Actually, no variation of thickness was taken into account in the EIS data processing.



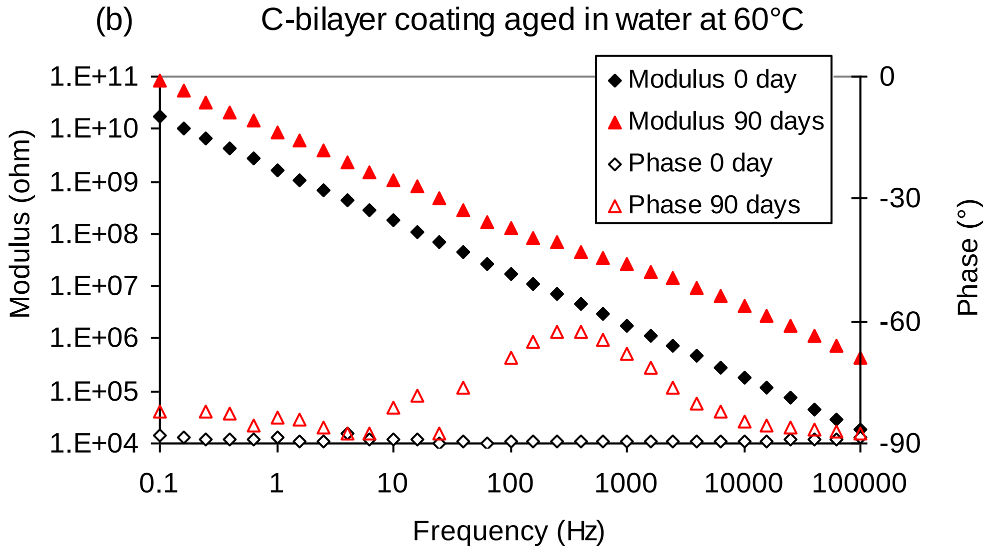


Figure 6 - Evolution with ageing time of the Bode plots for (a) B-bilayer coating and (b) C-bilayer coating

In conclusion, EIS results show that damages occurring in B-bilayer coating seem to be less harmful on the impedance response than those occurring in C-bilayer coating. The formation of water blistering in sub-layers in the later case only could explain those observations. Unfortunately no microscopic observation was done to confirm this interpretation. The differences observed between both bilayers are not fully understood yet.

4. Conclusions

This paper examined the use of Electrochemical Impedance Spectroscopy (EIS) to monitor durability and anticorrosion properties of three-layer coatings while exposed to water at 60 °C (maximum service temperature).

The use of EIS to quantitatively evaluate the water uptake kinetics in FBE primer coatings was investigated. The knowledge of water ingress kinetics is an issue to propose a reliable modeling of the water diffusion process into 3LPO coatings. It was shown that the use of EIS to monitor the water uptake in FBE primer having initial Tg around 100°C should be limited to lower temperature range than 60°C. However, future works to characterize the water uptake of novel high Tg FBE primers should, again, investigate the potentiality of EIS at 60°C or more. Expected benefits from EIS are in situ monitoring, continuous recording, and time saving in comparison to the classical gravimetry.

In addition, EIS appeared to be an appropriate method to detect sub-layer blistering in FBE/adhesive bilayer coatings, even though no macroscopic defect occurred through it (i.e. there is no path flow for the electrolyte to the metal surface). But EIS is obviously not sensitive to the formation of corrosion products at the pipe surface. Further work is in progress to model the EIS spectra by equivalent electrical circuits in order to improve the understanding of 3LPO degradation mechanisms.

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