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Contribution to a better FBE selection for 3 layer polyolefin coatings

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ABSTRACT

Recent case studies reported large scale disbondments of three-layer polyolefin (3-LPE) coatings, which could favour corrosion beneath the coating and lead to possible major damage. Therefore, it is necessary to better investigate the adhesion strength of fusion-bonded epoxy (FBE) primer to steel taking into account the water diffusing through the topcoat within the lifetime of pipeline.

A methodology was developed to examine the adhesion of sublayers to steel under wet exposure: peel tests were carried out on pipe rings industrially coated with FBE and adhesive layers only, aged in vapour to simulate the water ingress through the topcoat. This methodology could be included in selection or pre-qualification tests.

1 BACKGROUND

Among the two great families of external coatings of pipelines - FBE coatings and 3-LPE - each one has its advantages and disadvantages. In both cases, FBE is applied in direct contact to the freshly grit blasted pipe in order to provide good anchoring to steel.

1.1 FBE as external coating

As an example, FBE are appreciated because they are considered as fail safe (1). In other words, if FBE coatings are disbonded, they are not shielding, because their electrical resistance is low enough to allow cathodic protection (CP) to prevent corrosion of pipe. One must consider the origin of these electric resistances, which are sufficient to reduce the current demand considerably but low enough to let the current pass through it. In fact, at the time of the synthesis of the monomers, in particular of epoxy, the stages of alkaline neutralisation lead to the NaCl formation. This sodium chloride is washed out but remains with the concentration of some ppb. Thus the ions present in the epoxy resin confers a resistance of

some $10^8 \Omega.m^2$ at the dry state and low temperature to a resistance of few $10^2 \Omega.m^2$ for temperatures close to the glass transition temperature (T_g) and/or at the wet stage. One of the disadvantages is a greater brittleness at the time of handling and installation.

1.2 Three layer polyolefin as external coating

Polyolefins offer the advantage of a much less brittle material during installation: they offer a good mechanical protection with respect to the internal layers and in particular the FBE. However, the polyolefins contain only very few ions contrary to the epoxy resins; thus they have a very large electric resistance and they can lead to shielding effect, in particular in onshore application. Some water can flow along the metal surface and because of the high dielectric strength of polyolefin, CP current is unable to reach the pipe surface. Kehr roughly estimates that CP protects pipe underneath coating a distance of 3 to 10 times the distance between pipe and disbonded coating (1). But this statement obviously depends on the water conductivity: if pipe is offshore pipe, shielding effect is unlikely to occur (2) and recent laboratory results showed the same tendency (3, 4). .

1.3 Recent studies

Recent case studies reported large scale disbondments of 3-LPE coatings, which could favour corrosion beneath the pipe coating and lead to possible leakage or other major damage (2, 5, 6). In order to overcome this problem, a better understanding of disbonding mechanisms is necessary. A large parametric study was launched by GDF (7) using a specific testing device developed for plant applied extruded 3-LPE coating systems (8). Scarified 3-LPE coated pipe rings were aged under various conditions, then peeled off with an original protocol adapted from standard NF A49-710 to discuss the respective influence of cathodic potential, electrolyte conductivity and electrolyte circulation on long term 3-LPE adhesion to steel. However, the influence of FBE wet ageing on adhesion performance could not be distinguish from cathodic disbonding mechanisms. But pre-aged FBE coatings, e.g. exposed to water for a long period, may give larger disbonded area. In addition, the polyolefin has a very harmful role, which is unfortunately and regularly underestimated: it works as a permselective membrane, i.e. only the molecules such as water, oxygen, carbon dioxide diffuse but ionic species remain in the external medium. This can induce a catastrophic osmotic pressure effect which results in an increased water uptake in the FBE layer, that can undergo from internal blistering up to partial or total dissolution depending on the epoxy chemistry. These possible phenomena related to FBE wet ageing will considerably reduce the adhesion .

1.4 Pre-qualification tests (PQT)

3-LPE coatings are currently specified in the oil, gas and water pipeline industries. However, industrial practices for the selection, application and quality control of 3-LPE coatings hardly ever consider moisture induced adhesion loss of the FBE layer. As a matter of facts, the complete set of PQT on 3-LPE coated pipes usually comprises:

- thickness measurement,
- holiday testing,
- impact resistance,
- adhesion test,
- indentation,
- coating resistivity,
- elongation of the polyolefin layer,
- thermal and UV ageing,

- cathodic disbondment.

These methods are well described in standard documents, for example NF A 49-710 or DIN 30670 for polyethylene (PE) and NF A 49-711 or DIN 30678 for polypropylene (PP). Adhesion tests are performed on production rings. Cathodic disbondment test also characterises adhesion properties, but in the particular case of cathodic protection while water directly enters the macroscopic defect intended through the coating. Then, it is clear that none of the proposed tests address the risks of long term adhesion loss of the FBE when wetted by permeated moisture. Therefore, selection or pre-qualification tests should include soaked test not only to detect surface contamination/pollution, good coating application/cure but also resistance to osmotic pressure - to test the long-term adhesion performance of the FBE primer layer. But immersion tests on 3-layer systems could be too much time demanding. Moreover, the permeation through the polyolefin topcoat may mask differences among FBEs in too short term tests. Then, under layers (FBE and adhesive) should be inspected as stand-alone systems to provide relevant data to service conditions.

1.5 Water permeation through polyethylene top-coat

Polyolefin are semi-crystalline thermoplastics used as top-coat in 3-LPE coating systems to provide toughness and good damage resistance. Their barrier properties depend on their molecular structure and operating conditions. In a general way, the permeation of small molecules through polymers depends on both their solubility and diffusion coefficients. The permeability of a molecule through a polymer is defined by (9):

$$Pe = D.S$$

with S the solubility coefficient given in $\text{m}^3.\text{m}^{-3}.\text{Pa}^{-1}$,
 D the diffusion coefficient given in $\text{m}^2.\text{s}^{-1}$.

The coefficient of permeability of the main semi-crystalline materials used in the oil industries have been determined under a wide range of pressure and temperature in the IFP laboratories (10). Results concerning the polyethylene permeability towards water are given in Table 1 (11).

Taking into consideration a high density PE (HDPE) membrane exposed to liquid water on one side, it is possible to calculate the time necessary for a given amount of water to diffuse on the other side under given conditions, under the hypothesis of a steady state unidirectional diffusion regime, using the relation (11):

$$Pe = \frac{Q \times l}{t \times A}$$

with Q the amount of water in kg,
 l the thickness of membrane in m,
 t the time in s,
 A the polymer membrane area to cross in m^2 .

As an example, at 60°C, only 267 days are necessary to fill a 100×10^{-6} m gap between a top-coat (3×10^{-3} m thick) and steel pipe. This preliminary calculation has been reinforced by unidirectional modelling of water diffusion according to Fick's law (9) through a complete 3-LPE coating system, at both 60°C and 20°C. 3-LPE coating systems under consideration were

typically industrial systems similar to those called "type A" in the experimental part of this work. Concentration of water at saturation and diffusion coefficients used for modelling are summarised in Table 2.

The water concentration profiles in 3-LPE modelled after various times at 20°C and 60°C are illustrated, respectively, on Figure 1 and Figure 2. The saturation level in the FBE layer should be reached within one or two years time, under isothermal conditions investigated. This modelling underlines that the intrinsic permeability of polyethylene to moisture does not prevent water ingress into sub layers (adhesive and primer layers) within the life time of pipeline. This phenomenon will affect the adhesion performance of the primer layer to the steel (wet ageing), which is a crucial functionality required from coating along the pipe lifetime.

In this work, a methodology was developed to examine the strength of the bond between steel and primer layer taking into account the water diffusion through the PE top-coat. The coating application protocol was to subdivide a steel pipe into three parts: one coated with only FBE, the second with FBE + adhesive and last with the 3 layers during the same application run. The main objective of the work was to submit bi-layer coating (FBE + adhesive) systems to humid atmosphere to simulate the high purity water ingress through the top-coat. Besides, cathodic disbondment tests were also carried out on scarified three-layer coated pipe rings. This methodology is then discussed as an additional test during selection or PQT or even production tests.

2 EXPERIMENTAL SECTION

2.1 Coating composition and application

The steel preparation and coating application were performed in a plant according to GDF specification SPEC PC Rv 06 on a 6 m long steel pipe. Bi-layer and three-layer coated pipe rings (0.11 m diameter and 0.3 m long) are presented in Figure 3 as received. Rings named "A" had a 70×10^{-6} m thick FBE primer and "B" a 100×10^{-6} m thick FBE primer. The related 3-LPE systems are called, respectively, A-3LPE and B-3LPE in this paper.

2.2 Ageing conditions

In the case of bi-layer coating systems, ageing were performed at 60 °C on rings as received exposed in a specific cell (Figure 4) to 95 % relative humidity vapour following standard DIN 50008 to simulate the electrolyte filtered by the PE top-coat. In the case of 3-LPE coatings, ageing at 60 °C were performed on pipe rings immersed in 3 % NaCl water scarified every 28.10^{-3} m until steel and submitted to cathodic protection by potentiostatic polarisation (-1,1 V vs. Ag/AgCl). Note that the graphite counter electrode was 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.

2.3 Peel tests

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). Note that a counter roller maintained a constant peel angle of 90 degrees (8).

3 RESULTS

3.1 3-LPE coating systems

Peeling off 3-LPE coating at the initial state (e.g. production ring) was very difficult due to the high level of adhesion for FBE primer to steel. In most cases, PE failure (cohesive) occurred preferentially to 3-LPE disbonding. Nevertheless, it was possible to measure an average peel strength on a very short displacement (Figure 5). The peel energy calculated by dividing the peel strength of 800 N by the band width is $29 \times 10^3 \text{ J.m}^{-2}$ which is in agreement with values reported in the literature (8).

As an example, the peel test of aged 3-LPE coating is illustrated in Figure 6 after three weeks immersion in 3 % NaCl solution under cathodic protection. Two areas can be observed from the peeled strip as previously reported in the literature (7, 8):

- the exterior areas exhibiting pure adhesive failure (at steel/epoxy interface) that can be attributed to cathodic delamination in the vicinity of the scarified metal;
- the central area exhibiting cohesive failure may be affected by wet ageing only. Therefore, the width of the central area should be the width taken into account to calculate the peel energy along ageing and discuss the evolution of the bonding strength between steel and primer layer due to water diffusing from scarified defects.

Results after 21, 28 and 42 days ageing are reported in Table 3. It appears that this calculation of peel energy is almost impossible when the recorded strength values are highly dispersed and the adhesive band width is discontinuous. This happened in most cases with the thin primer A, showing one limit of this method of characterisation. In addition, such a testing protocol applied on scarified 3-LPE under cathodic protection does not allow to discuss the wet ageing of the adhesive bond between FBE primer and steel properly, due to overlapping of both cathodic disbonding and wet ageing mechanisms.

3.2 FBE/adhesive coating systems

The peel test applied to the bi-layer coating is illustrated on Figure 7. A strip of $20 \times 10^{-3} \text{ m}$ width was cut just before the peeling test. By performing some knife cut within the bi-layer coating, it was noticed that adhesive separation occurred systematically after a few days ageing at 60°C . One should note that metal appeared white under the peeled area whatever the case. The peel strengths recorded at various ageing time for both A and B bi-layer coatings (see Figure 8 and Figure 9) are summarised in Table 4. Calculated peel energies are reported as well.

The peel strengths tend to decrease with ageing time, showing the progressive weakening of the adhesive strength from primer on steel due to wet ageing. Therefore, this new methodology gives a measure sensitive to wet ageing that could be reliable for FBE evaluation and selection. Comparison between A and B-bilayer systems also underlines the stronger adhesion to steel for the $100 \times 10^{-6} \text{ m}$ primer layer compared to the $70 \times 10^{-6} \text{ m}$ primer layer, whatever the ageing time. These results are two major outcomes of this work.

4 DISCUSSION

4.1 FBE pre-selection

To summarise, a methodology has been presented to study the wet ageing of the adhesion bonds between FBE primer and steel for 3-LPE coating systems. As was discussed above,

ageing on scarified three-layer coatings submitted to cathodic protection as described in international standard cathodic disbondment test cannot allow to discriminate properly between wet ageing and cathodic delamination mechanisms. Preliminary results showed that wet ageing was achieved in reasonable time tests through the study of primer/adhesive bi-layer coatings. In the particular example presented in this paper, bi-layer systems were exposed 6 weeks to 95 % relative humidity air at 60°C in order to simulate the water filtered by the top-coat. As a result, the FBE adherence strength is measured by peeling during ageing, offering a unique and reliable manner to quantitatively follow the weakening of FBE primer adherence due to wet ageing.

During FBE selection or pre-qualification, this methodology devoted to bi-layer coating systems can complete the testing method used to measure practical adhesion (peeling test) in comparison with the conventional method that is being used for stand alone epoxy primer layer, namely the pull-off test; or the adhesion rating as per Nace 0394-2002. Indeed, peeling a bi-layer strip with a hydraulic testing machine avoids the use of any adhesive to bond dollies to the wet coating that require time to cure and very caution handling to be sure a continuous film covers the entire surface - moreover trimming is claimed to create cracks within the system which are responsible for a large decrease in the measured parameters (12). Perhaps more important, though, is that the pull-off test on bi-layer coating will be able to effectively evaluate adhesion strength on industrially coated prototypes whereas pull-off tests specified by ISO 4624 are recommended on flat samples. However, during production, the hot water soak test described in Nace 0394-2002 can be easily extended to the first two layers of 3 layer coating.

Modelling of water diffusion were conducted on bi-layer coatings exposed to water at 60 °C (Figure 10 and Figure 11). The objective was to determine the concentration profiles of water within the coating until saturation in order to discuss the experimental results obtained in very similar conditions (95 % relative humidity) after 21, 28 and 42 days. Both water profiles obtained after 10 days have reached their saturation level, assessing that the adhesive bonds between FBE and steel surface undergo wet ageing within the time of our experiences. The very short time required to reach the saturation that is necessary to investigate further ageing mechanisms is a clear benefit of the methodology described above. As a matter of fact, the pre-selection test devoted to the wet ageing assessment could last typically 14 days in water maintained at 60 °C minimum with thickness in the range of 100×10^{-6} m (parameter to adjust in function of service conditions).

4.2 FBE thickness

Several cases of loss of adhesion of FBE were reported in the literature due to water absorption during outdoor storage period (1, 13). Coated pipe storage in hot and humid atmospheres can conduct to a water uptake of FBE at cut back and through bulk polyolefin.

Initially, FBE was applied to a low thickness to ensure a good anchoring of top coat to steel. Recently, from bad field experiments, this view is falling out of favour, and now thicker layers are specified from 150×10^{-6} m for ambient temperature to 400×10^{-6} m for higher temperature. Use of thicker FBE layer goes into a higher anticorrosion protection and higher adhesion. However, Norman has recently reported blistering phenomenon during field joint coating (14). This blistering is generally explained through problems during coating application/cure or surface preparation. However, water uptake should also be considered, because a thicker coating will absorb more water, and thus drying operation is more difficult (to triple the thickness multiplies by nine the duration of drying), in particular during fast

heating operation, when the desorption of the water contained in the coating will be able to cause blisters. This is a point to keep in mind when specifying the thickness of the FBE, concomitantly with the chemistry of resin (e.g. its water uptake at the temperature and hygrometry of storage once applied).

5 CONCLUSIONS

From this study, it can be clearly concluded that the bonding strength of FBE primer to steel can be sensitive to wet ageing due to water diffused from external exposition. This water diffusion through any polymeric top-coat is expected within the lifetime of pipe, according to permeability data. Thus, an additional methodology based on the ageing of bi-layer FBE/adhesive coatings is proposed to provide an accelerated evaluation of the FBE adhesion to steel during wet ageing. Indeed, the first step associated with water diffusion through the polyolefin top-coat is suppressed. This methodology will allow to discuss the influence of external damaging factors (medium, temperature) but also intrinsic material factors (epoxy chemistry, layer thickness) on the bonding strength between steel and FBE primer layer.

Since a good resistance of the coating-to-steel adhesion is mandatory for the long term performance of 3-LPE, the methodology proposed could help designers and operators to select a FBE primer chemistry and thickness in complement to traditional testing protocols dedicated to 3-LPE under CP and including an artificial defect within the coating.

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Table 1- Water permeation results for HDPE (11)

Temperature (°C)	Thickness $\times 10^{-3}$ m	Permeability $\times 10^{-11}$ kg.m/m ² .s
40	0.52	0.3 ± 9 %
53	0.52	1.0 ± 8 %
60	0.55	1.3 ± 4 %
80	0.54	5.5 ± 1 %

Table 2- Water diffusion coefficient and concentration at saturation in a 3-LPE system

Layer	Diffusion coefficient ($\times 10^{-12}$ m ² /s)		Concentration at saturation (%)		Origin
	20°C	60°C	20°C	60°C	
HDPE	1.2	14	0.1	0.1	IFP data
Adhesive	0.34	4	0.5	0.5	IFP hypothesis
FBE	6.10^{-3}	7.10^{-2}	2.0	6.0	IFP data

Table 3 - Evolution with time of the peel strength (mean value), the adhesive band width (mean value) and peel energy for A and B 3-LPE coatings aged in 95 % relative humidity at 60°C

Ageing time (days)	A-3LPE coating			B-3LPE coating		
	Strength (N)	Adhesive band (m)	Peel energy $\times 10^3$ J/m ²	Strength (N)	Adhesive band (m)	Peel energy $\times 10^3$ J/m ²
0	800	0.028	29			
21	50 to 300	0 to 0.011 discontinuous		200-500	0.010 regular	20-50
28	10 to 300	0 to 0.008 discontinuous		< 300	0.008 regular	< 37
42	< 10	None		< 15	0 to 0.005 discontinuous	

Table 4 - Evolution of the mean strength with time for A and B bi-layer coatings aged in 95% relative humidity at 60°C

Ageing time (days)	A-bi-layer coating		B-bi-layer coating	
	Strength (N)	Peel energy $\times 10^3$ J/m ²	Strength (N)	Peel energy $\times 10^3$ J/m ²
0	No measure	-	No measure	-
21	6.0	300	7.5	375
28	6.0	300	7.5	375
42	2.0	100	5.0	250

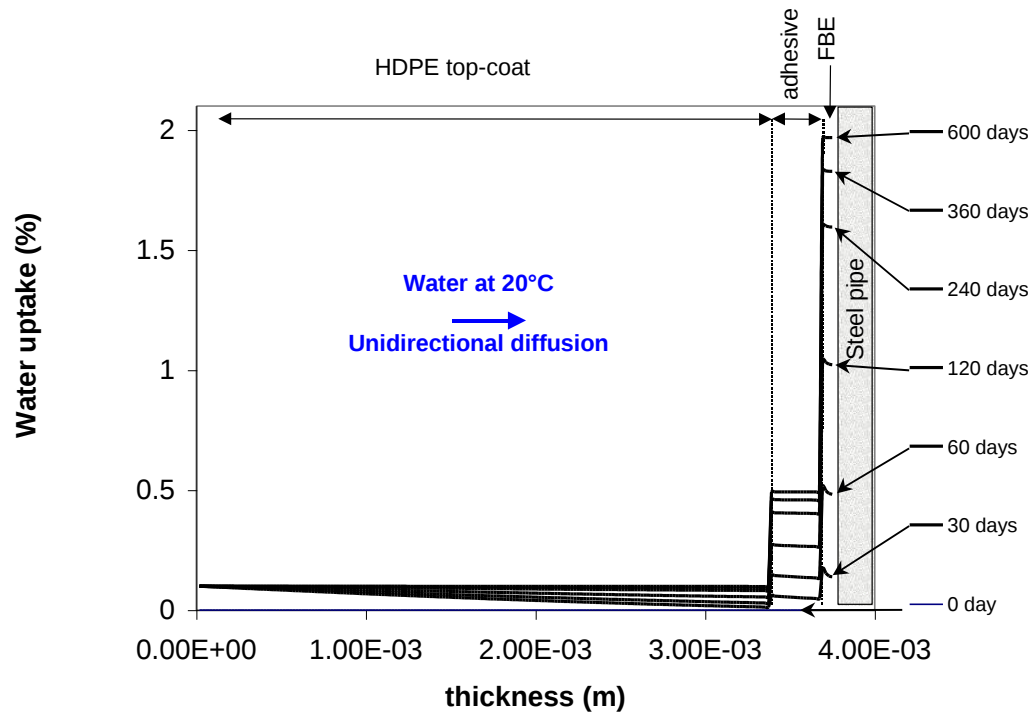


Figure 1 - Water concentration profiles in 3-LPE (type A) exposed to water at 20°C

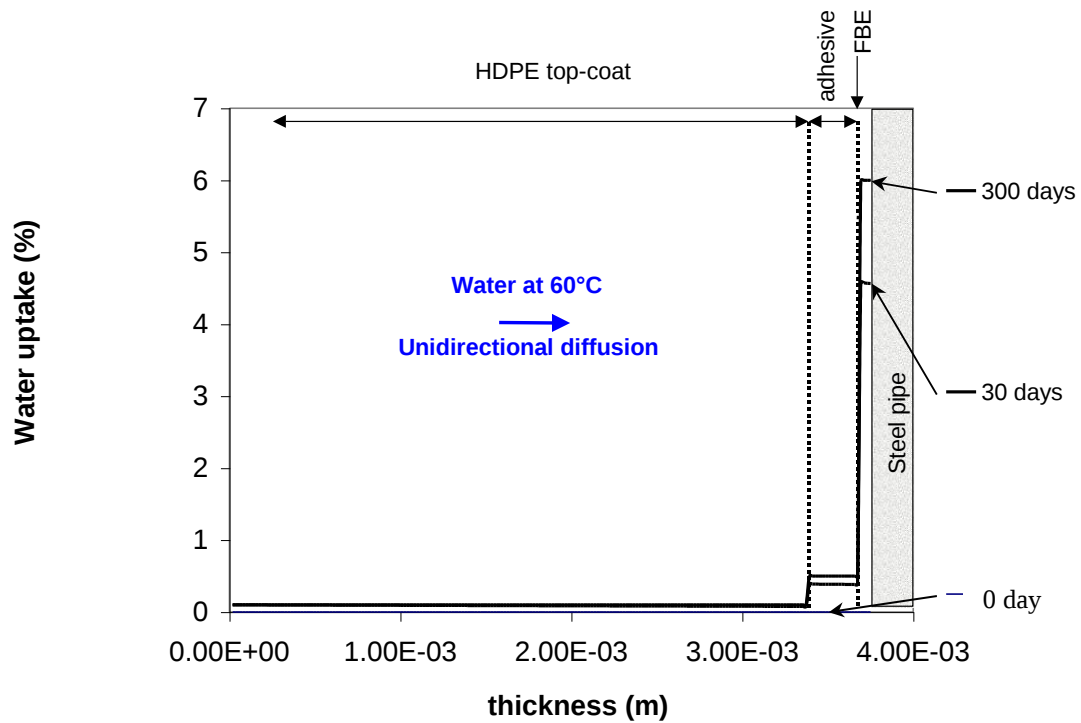


Figure 2 - Water concentration profiles in 3-LPE (type A) exposed to water at 60°C



Figure 3 - 3-LPE tubes (on the left) and bi-layer tubes (on the right) as received



Figure 4 - Illustration of an ageing cell

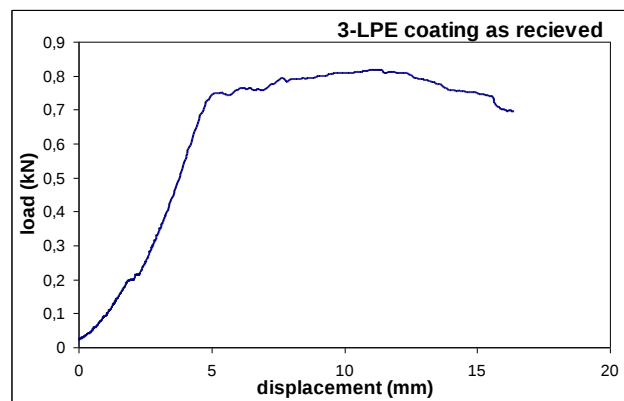


Figure 5 - Peeling of the B-3LPE coating as received



Figure 6 - Peeling of the B-3LPE coating aged 21 days in 3 % NaCl solution under -1,1 V vs. Ag/AgCl

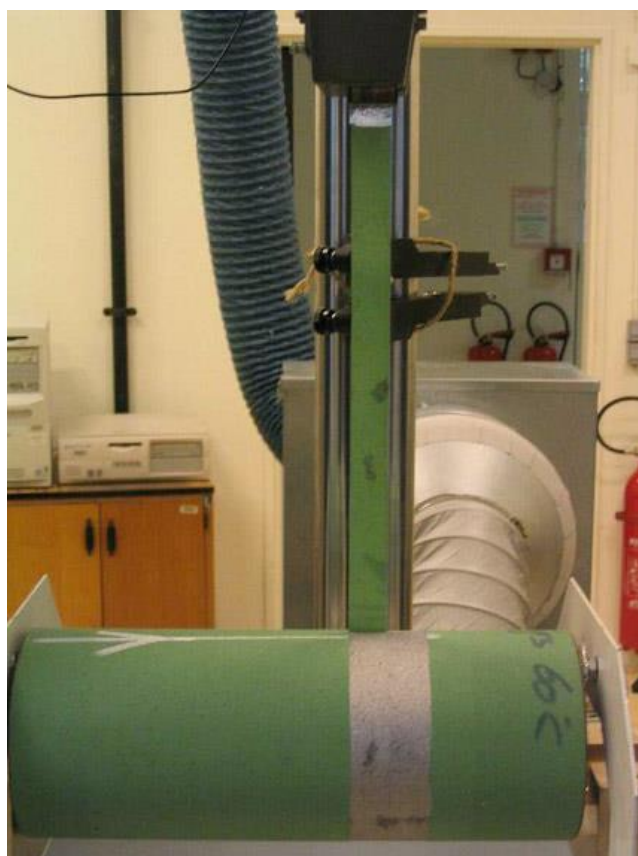


Figure 7 - Peeling of the bi-layer coating after a few weeks ageing at 60°C

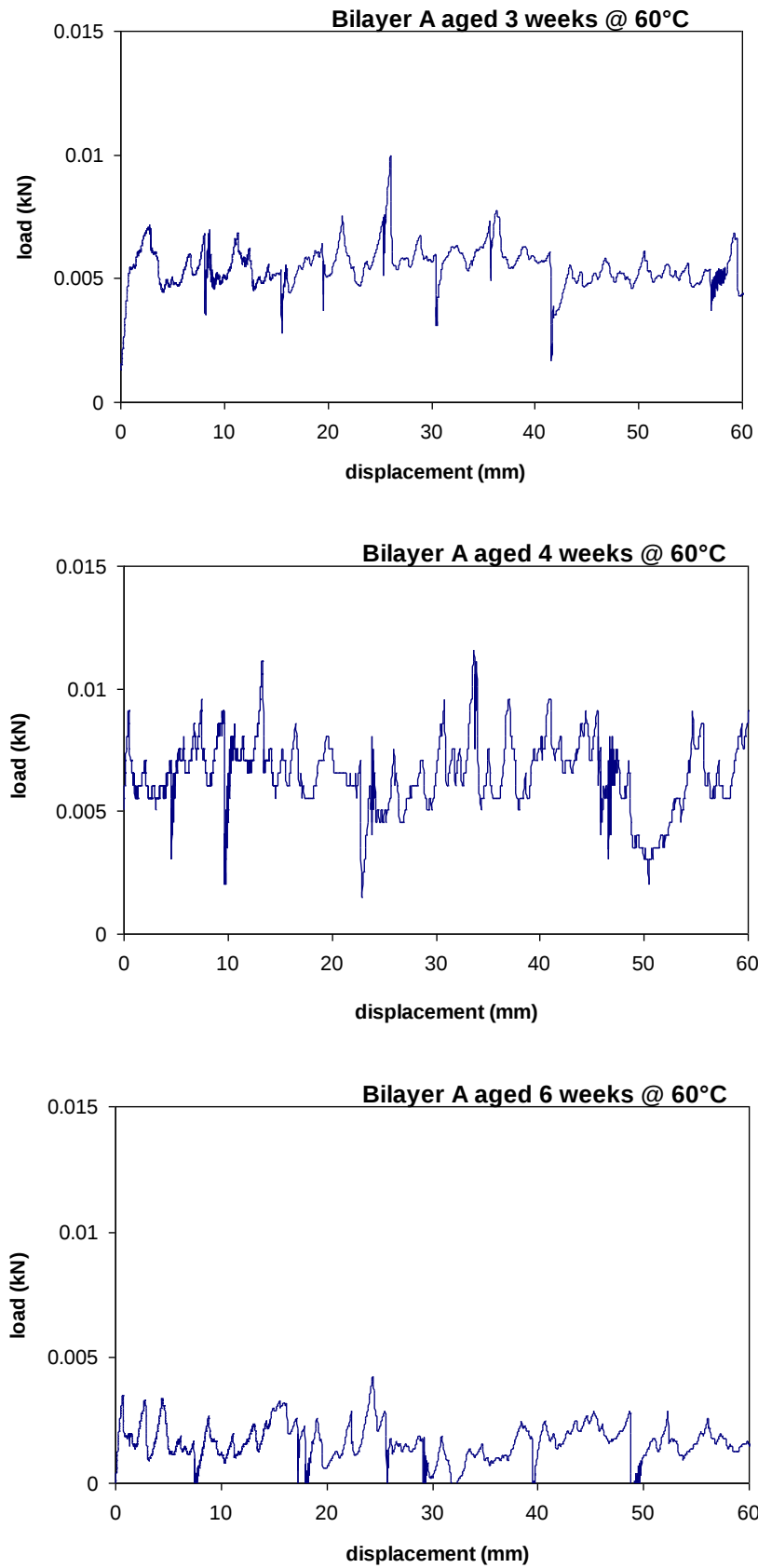
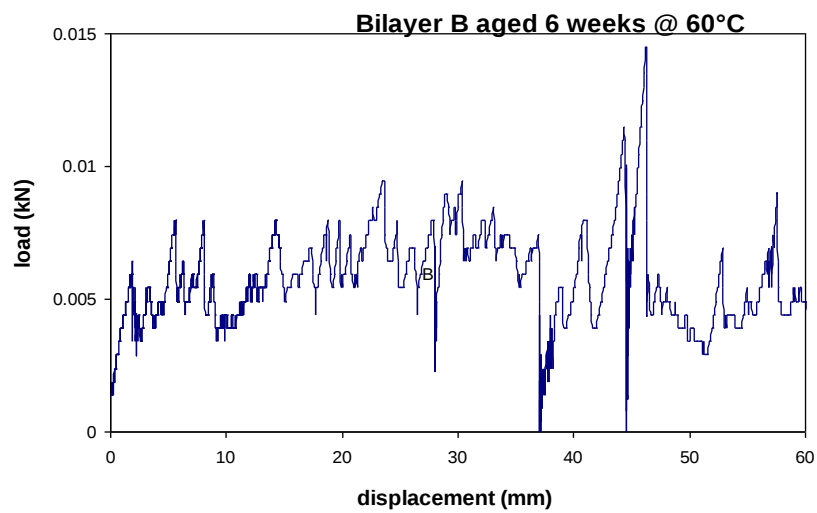
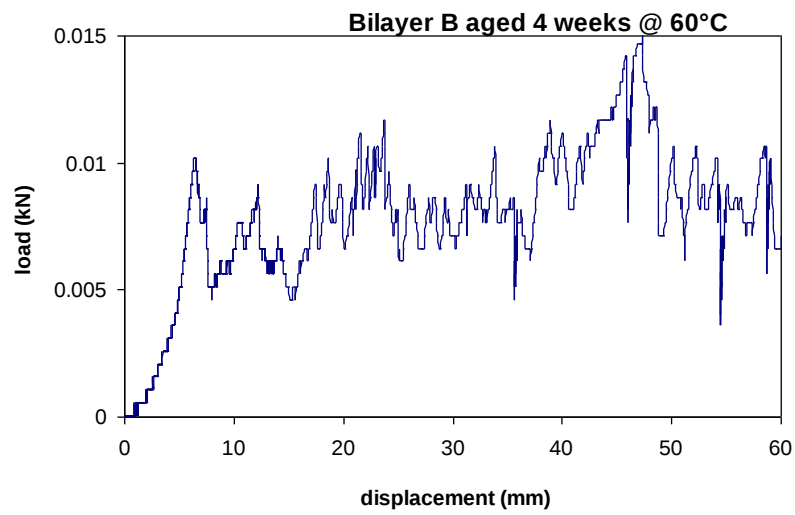
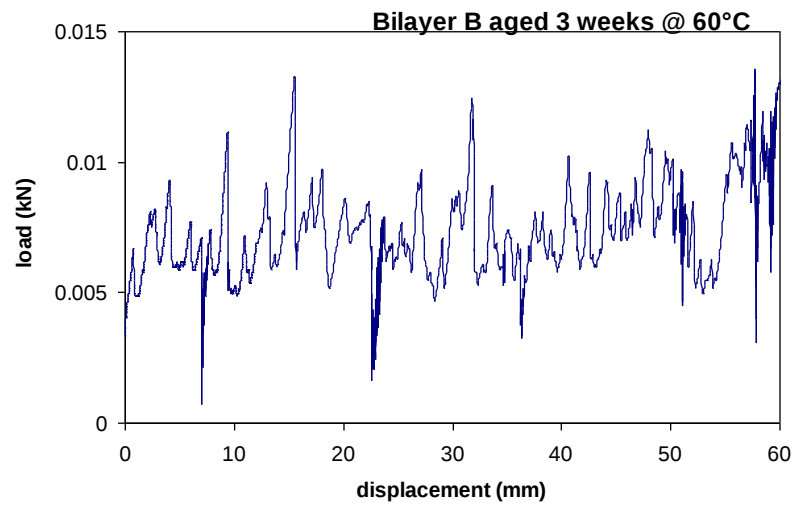


Figure 8 - Peeling of A-bi-layer coating exposed to 95 % relative humidity at 60°C: results after 3, 4 and 6 weeks



**Figure 9 - Peeling of B-bi-layer coating exposed to 95 % relative humidity at 60 °C:
results after 3, 4 and 6 weeks**

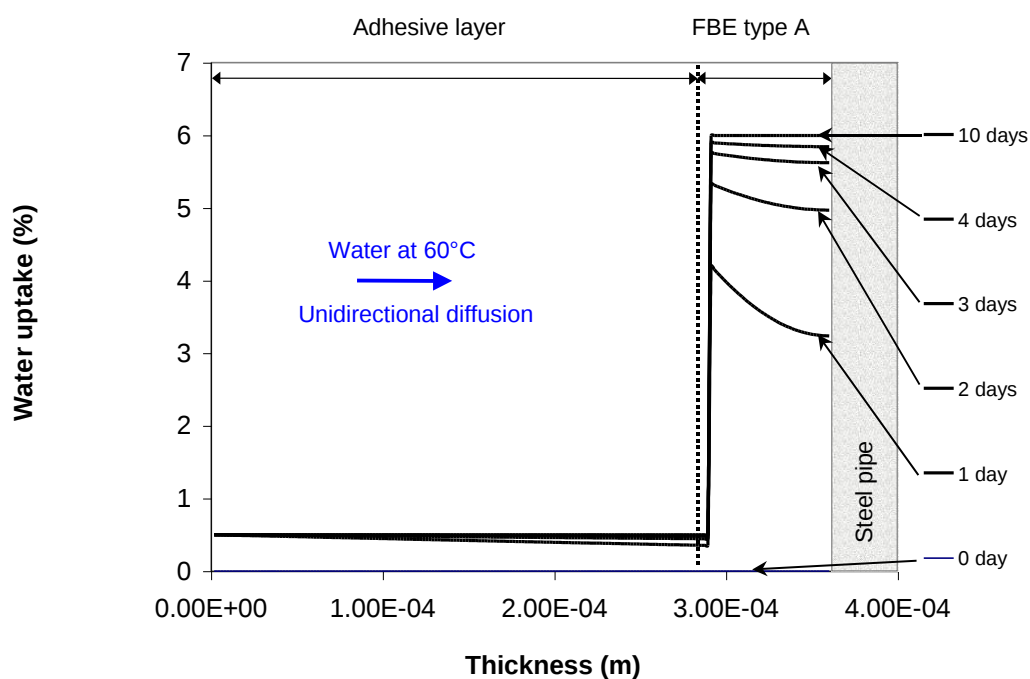


Figure 10 - Water concentration profiles in bi-layer (type A) coating exposed to water at 60°C

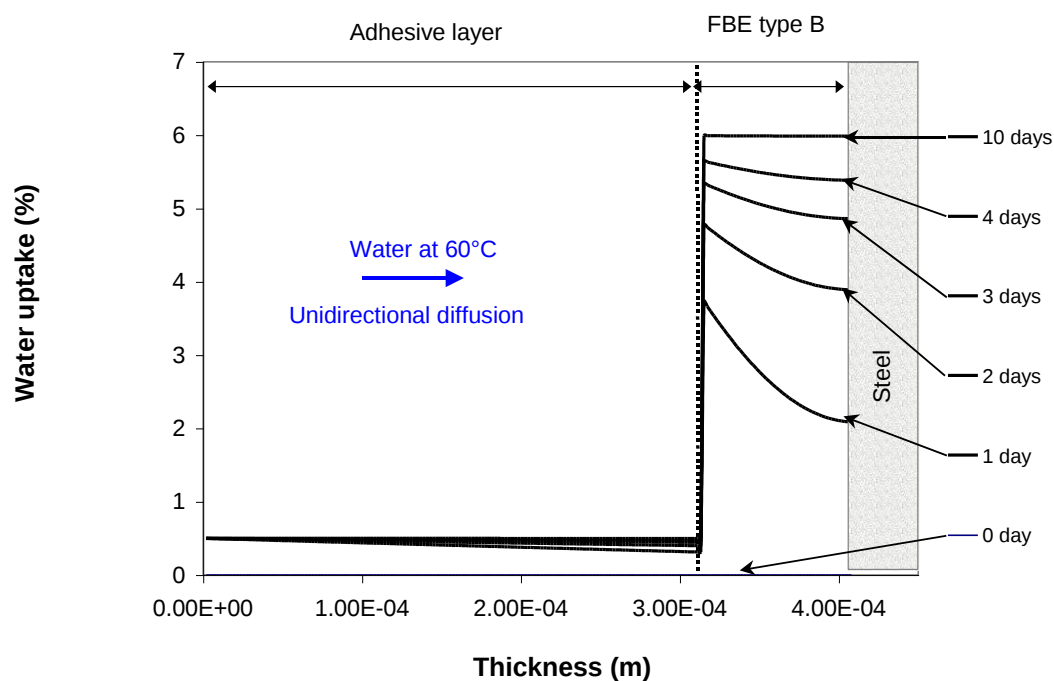


Figure 11 - Water concentration profiles in bi-layer (type B) coating exposed to water at 60°C