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# Hot wet ageing of glass syntactic foam coatings monitored by Impedance Spectroscopy

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## **Abstract**

Syntactic foam coatings have been used extensively over the past decades in the oil and gas industries for many purposes. They are based on glass hollow microspheres embedded in an organic matrix, building a closed-cell structure suitable for applications in marine environment. Syntactic foam coatings are expected to fulfil today's challenges as pipelines are required to operate in more and more difficult conditions, namely under the combination of high pressure & high temperature conditions (up to 300 bar / 130°C). They are being used to provide buoyancy up to deep water but also thermal insulation as well as corrosion protection while being cast directly on a steel pipe. Therefore, there is a need of a better knowledge of technical performance and limitations of syntactic foam coatings exposed to so called "hot wet" environment which can induce rapid and severe degradation, damaging the coating efficiency in terms of sustainable insulation and protection.

This paper examined both short and long term behaviours of glass-epoxy syntactic foam coatings including various types of microspheres while exposed to hot distilled water. Impedance Spectroscopy was used to in situ monitor the water uptake of the coating in complement to gravimetry but also to investigate the degradation phenomenon occurring after matrix had reached saturation (monitoring over 10000 hours). Diffusion properties were discussed from capacitance measurements. In addition, attention was paid to the increase of ionic conductivity suggesting the occurrence of ionic extraction from the microsphere glass due to water leaching. Possible degradation mechanisms were discussed from the results obtained by in situ technique in comparison to classical gravimetric data. The interest of impedance spectroscopy for the investigation of composite coating ageing was highlighted.

**Keywords:** organic coating, glass composite, ageing, impedance spectroscopy

## **INTRODUCTION**

Syntactic foam coatings have been used extensively over the past decades in the oil and gas industries for many purposes. They are based on glass hollow microspheres (diameters ranging from 10 µm to 100 µm) embedded in an organic matrix, building a closed-cell structure suitable for applications in marine environment. Syntactic foam coatings are expected to fulfil today's challenges as pipelines are required to operate in more and more difficult conditions, namely under the combination of high pressure & high temperature conditions (up to 300 bar / 130°C). While being cast directly on a steel pipe, syntactic foam coatings are being used to provide buoyancy up to deep water but also thermal insulation as well as corrosion protection - for a typical service of 20 years. Therefore, there is a need of a better knowledge of technical performance and limitations of syntactic foam coatings exposed

to so called "hot wet" environment which can induce rapid and severe degradation, damaging the coating efficiency in terms of sustainable insulation and protection [1, 2]. In particular, a more fundamental approach is needed to understand how the hydrolytic aging of microsphere glass may reduce the durability of syntactic foams used in hot wet conditions.

This paper focuses on the water uptake of model syntactic foam during aging in hot deionized water, monitored by Impedance Spectroscopy. Attention is paid to the electrical capacitance and conductivity changes, in complement to classical water sorption test on free standing films. Water diffusion and degradation mechanisms involved in syntactic foam during hot wet aging are investigated, discussed and compared to experimental aging data available on the pure polymer building the syntactic foam matrix. By formulating model syntactic foams with untreated glass microspheres embedded in an epoxy-amine matrix exhibiting stability in hot wet conditions, the influence of the glass hydrolytic aging can be studied rather properly.

The ultimate objective is to improve syntactic foam formulations that would enhance barrier properties and reduce possible irreversible damage in service conditions such as electrochemical activity at the pipe steel surface and breakage / filling of glass microspheres.

## **BACKGROUND**

### **Effect of water on electrical properties of polymers**

It has long been known that electrical impedance measurements can successfully monitor water diffusion into polymer membranes or coatings. High frequency capacity curves versus time can reveal the quantitative water uptake thank to Brasher's law [3], provided the experimental temperature is sufficient differing from polymer glass transition temperature [4, 5]. If phenomena are occurring in the same temperature range, the increase of the polymer permittivity of several units associated with the cooperative backbone mobility developed at the glass transition induces a capacity change that completely overwhelm the jump related to water uptake.

In addition, the electrical resistance of polymer membranes or coatings is known to decrease with water entrance. So far, changing the water activity is necessary to determine whether the resistance measured reflects the bulk polymer internal resistance or directly follows the solution resistance due to some porosity effect [6]: when the polymer resistance decreases with diffusing water irrespective of solution activity, conduction must involve internal ionic species present in the polymer [7] and whose mobility is related to polymer chain mobility. In the glassy state, there is only local mobility within epoxy-amine networks; therefore ion mobility through polymer coatings and membranes is limited and conductivity is very low. Matrix plasticization due to water uptake favors chain mobility, leading to a lowering of the glass transition temperature. Thus, some enhanced mobility is expected for internal ionic species as well, inducing an increase of the conductivity with water uptake.

In the present work, in situ electrical capacitance measurements during the initial stages of exposure to hot deionized water is used in complement to gravimetry to investigate the water transport in glass/epoxy syntactic foam. In addition, electrical conductivity changes give another distinct type of response, related to plasticization and other aging mechanisms, in particular leaching of glass ions.

## EXPERIMENTAL

### Material

Syntactic foam preparation has been detailed elsewhere [8]. The matrix consisted of a stoichiometric mixture of a difunctional epoxy resin and a diamine hardener, leading to a high T<sub>g</sub> network after extensive cure (170°C). Filler materials used were untreated sodium-borosilicate based glass microspheres of two nature, called "A" and "B", but exhibiting almost comparable median diameter and true density (Table 1).

Table 1: Comparison between microsphere characteristics (from commercial data sheet)

Reference of foams' spheres	Mean external diameter (microns)	Mean glass thickness (microns)	Actual density (g.cm <sup>-3</sup> )
A	35	2	0.35
B	40	3	0.38

Extensive morphological control by 3D X-ray microtomography to assess material morphology is reported elsewhere [9].

For comparison purpose, pure epoxy-amine polymer was prepared following the same protocol. Parallelepiped samples of 50\*50\*2 mm<sup>3</sup> were cut for both gravimetric and impedance measurements.

### Aging

Isothermal aging experiments were carried out over 2 years at 22°C and 100°C in deionized water (~ 10<sup>6</sup> ohm.cm). Provided there is no concomitant mass loss from the aged sample, the water uptake in weight percent (wgt. %) was calculated from regular mass gain control on blotted dry samples, normalized by the initial mass.

### Impedance Spectroscopy

Impedance measurements were performed between 10<sup>5</sup> Hz and 0.1 Hz (3 measures for each control) with a sine wave of 100 mV using a Solartron 1260 FRA device equipped with a Solartron 1296 dielectric interface.

In situ impedance measurements at 100°C were carried out during the first hours of exposition to hot deionized water in a polypropylene aging cell (Area of 12.5 cm<sup>2</sup>). Both electrodes were hastelloy grids carefully pressed on each side of the sample surfaces building a traditional parallel-plate 2 electrodes set-up (Figure 1). Ionic conductivity was calculated from impedance data and sample geometry.

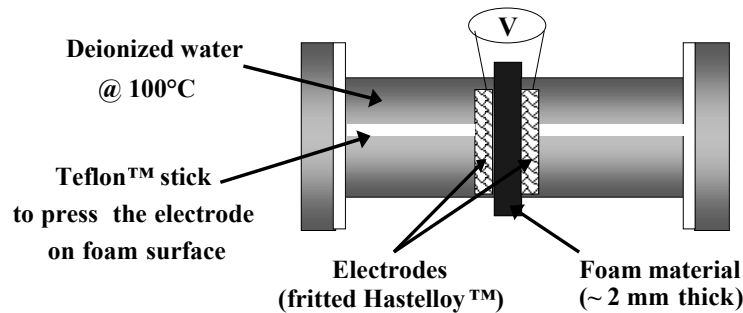


Figure 1 : Aging cell with two electrode set-up for water uptake monitoring at 100°C.

In addition, ex situ impedance measurements at 22°C were performed on gravimetric specimen aged in a separate vessel over months. A parallel-plate 2 electrodes set-up was also used. Note that water desorption during impedance measurement was checked to be negligible. Moreover, attention was paid to apply a low potential value and to avoid any perturbation that could provoke interfacial polarization or surface conduction effect [10].

## RESULTS AND DISCUSSION

### Hot wet aging for pure epoxy-amine polymer

The short term behavior in water of the pure epoxy-amine polymer under consideration as revealed by impedance spectroscopy is illustrated in Figure 2.

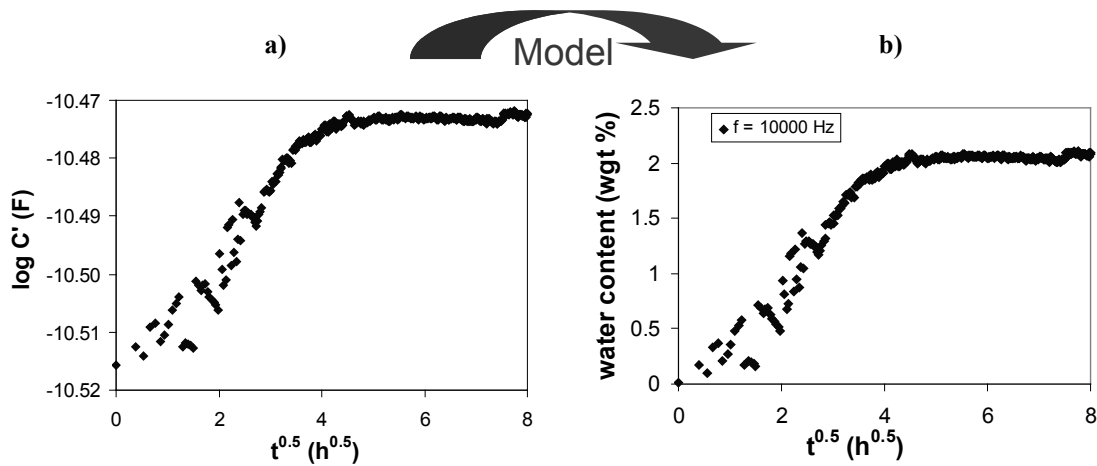


Figure 2 : Water uptake monitoring by EIS in the pure epoxy-amine polymer at 100°C; a) capacitance evolution with square root of time; b) water content given by EIS according to Brasher and Kingsbury law [3].

From the capacitance values at 10000 Hz, the water content evolution is calculated using the Brasher and Kingsbury law [3].

$$\phi = \log(C_t/C_0) / [\rho \log(\epsilon_w)] \quad (1)$$

where  $\phi$  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),  
 $\rho$  the density of polymer film,  
 $\epsilon_w$  the permittivity of water ( $\epsilon_w = 56$  at 100°C).

In a second step, diffusion coefficient  $D$  can be evaluated through equation (2) according to a Fickian behavior for the water absorption [11]:

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

where  $M_t$  is the mass of water absorbed at time  $t$ ,  
 $M_\infty$  is the mass of water at infinite time  $t \rightarrow \infty$   
 $l$  is the thickness of film.

Comparison between in situ impedance and ex situ gravimetry results for pure epoxy-amine polymer immersed in deionized water at 100°C are presented in Table 2.

Table 2: Comparison between ex situ gravimetry and in situ impedance monitoring of water uptake in pure epoxy-amine polymer immersed in deionized water at 100°C.

Water content at equilibrium (wgt. %)		Diffusion coefficient ( $\times 10^{11} \text{ m}^2/\text{s}$ )	
Gravimetry	EIS	Gravimetry	EIS
1.7	2.0	1.1	0.9

Diffusion coefficient and water content at equilibrium are in very close agreement. Thus, the capacity change is directly related to increasing material permittivity with water entrance (Figure 3).

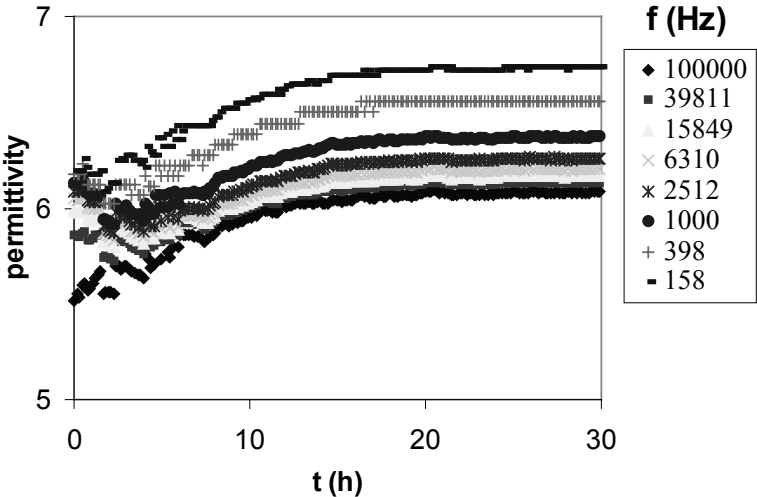


Figure 3 : Evolution with time of the permittivity of a pure epoxy-amine polymer exposed to deionized water at 100°C.

One should note that plasticized epoxy-amine under consideration admits a quite low water content in the saturated state (< 2 % wgt.). Its related wet Tg value is around 130 °C, i.e. sufficiently differing from the aging temperature to allow a quantitative use of Brasher law [4, 5].

**Hot wet aging of syntactic foams**

Figure 4 represents the mass gain for a 55 % vol. filled syntactic foam as a function of the square root of immersion time in deionized water at 22 °C and 100 °C during 18 months.

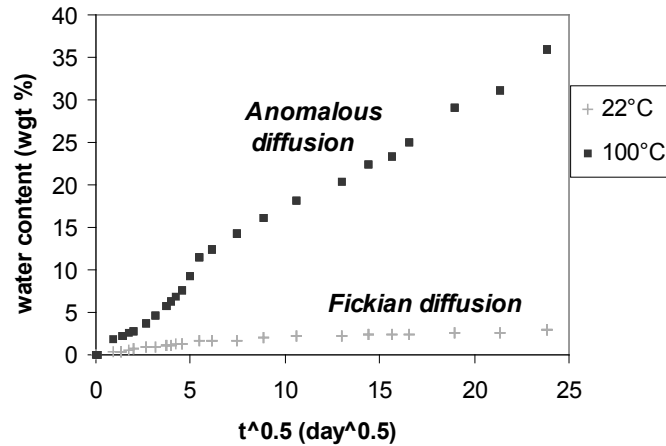


Figure 4: Typical water uptake behavior followed by gravimetry for a 55 % vol. syntactic foam immersed in deionized water at 22°C and 100°C.

The main observation is that the mass gain curve related to hot wet aging almost steadily increases with time and does not follow a classical Fick law, whereas the 22°C curve does. Indeed the 22°C curve presents a Fickian behavior over the aging time similar to pure epoxy-amine polymer. The water content at the plateau (~ 3 % wt) remains close to the saturated polymer water content, suggesting that long term aged syntactic foams at room temperature almost exhibits a saturated matrix. Besides, it is well known that water diffusion in the matrix is thermally activated, which could account for the different initial slopes observed when water uptake remains below 2-3 % wt. But other water diffusion mechanisms must be identified to explain the steady water uptake occurring in hot wet aging conditions. Since the volume expansion of one year aged syntactic samples is almost similar whatever the aging temperature is and remains inferior to 5 %, it seems obvious that water does not only hydrate the polymer matrix but possibly also hydrates the microsphere interfaces, the glass material and/or fills in microspheres as well.

Impedance spectroscopy is proposed as a new method for further investigation and discussion on these possible mechanisms. Impedance monitoring of the 55 % vol. syntactic foam A exposed to deionized water at 100 °C is illustrated in Figure 5.

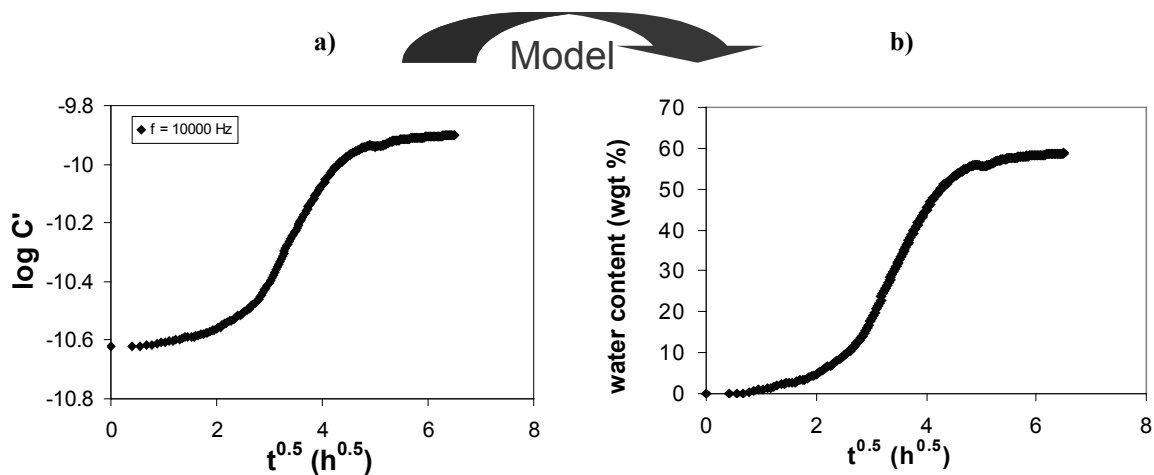


Figure 5 : Water uptake monitoring by EIS in the 55 % vol. syntactic foam at 100°C; a) capacitance evolution with square root of time; b) water content given by EIS according to Brasher and Kinksbury law.

The inspection of the capacitance values at 10000 Hz clearly points out that the water uptake evolution does not follow a simple Fickian law, on the contrary to pure epoxy-amine polymer. Indeed, the use of Brasher and Kingsbury law (1) leads to very overestimated water uptake values, since gravimetry measurements give 2.7 % water content by the end of the impedance test.

The inspection of permittivity data highlights the occurrence of an additional polarization effect, as revealed by the massive permittivity increase observed after ~ 5 hours exposition whatever the frequency, but higher at lower frequencies (Figure 6).

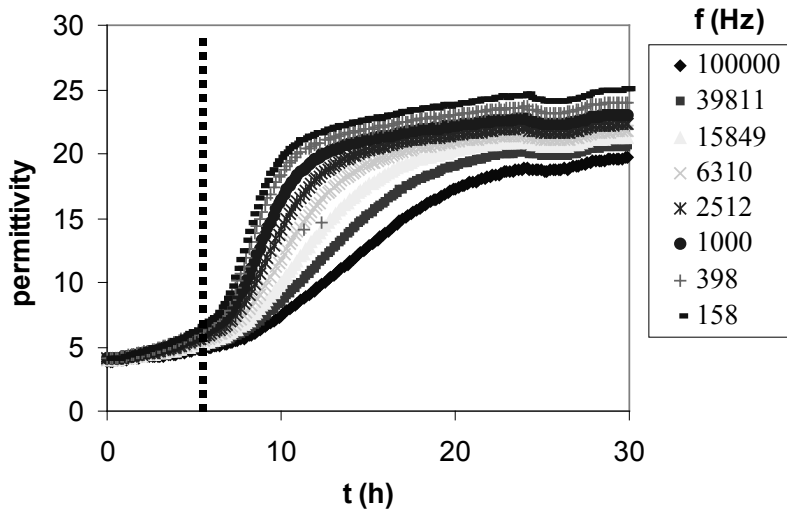


Figure 6 : Evolution with time of the permittivity of a 55 % syntactic foam exposed to deionized water at 100°C.

This phenomenon could be attributed to an interfacial polarization on the glass microspheres occurring as soon as matrix is fully plasticized. Therefore, simulations were performed to determine the water concentration profiles within syntactic foam under consideration on the basis of a Fickian behavior, using Crank [11] equation (3):

$$C(x) := 1 - \frac{4 \cdot \sum_{n=0}^{50} \frac{(-1)^n e^{-\frac{(-1) \cdot D \cdot (2n+1)^2 \cdot \pi^2 \cdot t}{4l^2}} \cdot \cos\left[(2 \cdot n + 1) \cdot \pi \cdot \frac{x}{2 \cdot l}\right]}{(2 \cdot n + 1)}}{\pi} \quad (3)$$

with  $C(x)$  the concentration at the depth  $x$ ,  
 $l$  the half thickness of the sample,  
 $D$  the diffusion coefficient in the material ( $D_{100^\circ\text{C}} = 3.9 \cdot 10^{-12} \text{ m}^2/\text{s}$  [12]).

According to concentration profiles (Figure 7), 5 hours exposition corresponds to the time when both diffusion fronts meet in the middle plane: the generalized mobility increase associated to matrix plasticization favors interfacial polarization on glass microspheres [13].



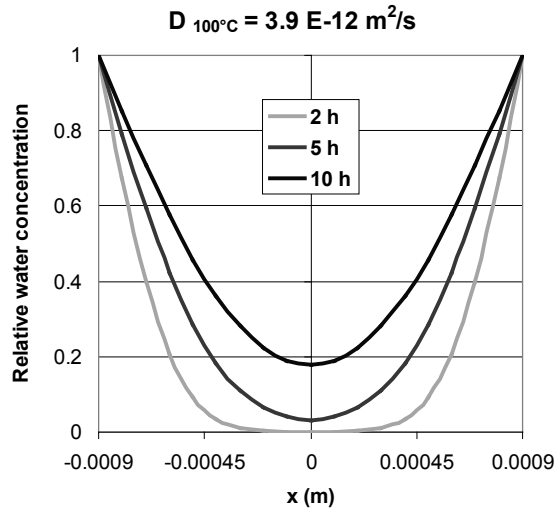


Figure 7 : Water concentration profiles within a 55 % vol. syntactic foam "A" at 100°C.

### Influence of glass nature

The ionic conductivity calculated from in situ impedance measurements during immersion in deionized water at 100°C is represented as a function of the normalized square root of time on Figure 8 for both 55 % vol. syntactic samples under consideration. Results of the pure epoxy-amine polymer are also represented for comparison purpose.

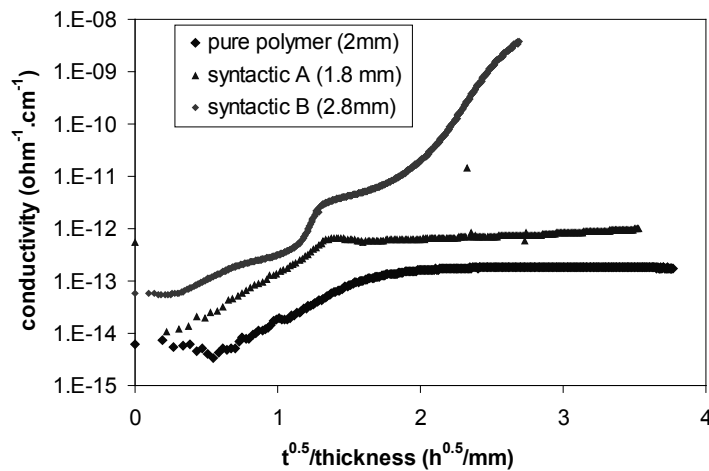


Figure 8 : Conductivity evolution with square root of time normalized by simple thickness for two 55 % vol. syntactic foams "A" and "B" exposed to deionized water at 100°C during 60 hours; comparison with pure epoxy-amine polymer.

The obvious differing behavior of syntactic foams after both diffusion fronts have merged underlines the influence of glass nature on the internal syntactic foam conductivity. Long term aging experiments at 22°C and 100°C were performed on both syntactic foams to discuss further this phenomenon. Ex situ impedance measurements at 22°C were performed during the long term aging at 100°C of both syntactic foam very regularly, in complement to gravimetric measurements. The representation of the conductivity measured at 22°C as a function of the mass gain on foam "A" aged at 22°C and 100°C in deionized water as illustrated on Figure 9 is proposed for a better understanding of possible water uptake mechanisms.

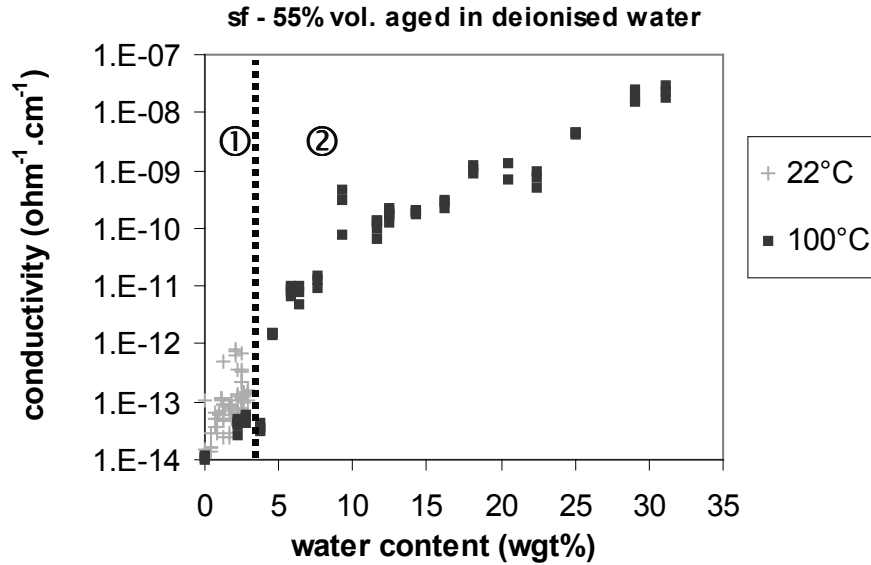


Figure 9 : Conductivity evolution with water content for 55 % vol. syntactic foam "A" exposed to deionized water at 22°C and 100°C during 18 months.

The syntactic material aged at 22°C exhibits a weak increase in conductivity (one decade) whatever the aging time. The water content remaining below 3 %, the matrix saturation is pointed out as the predominant governing factor of water diffusion into syntactic foams aged in deionized water at low temperature. The consideration of the conductivity evolution versus water uptake associated with hot wet aging points out a markedly different behavior. Both conductivity and water content increase significantly over the aging time, but there is no direct proportionality. A first interpretation can be the nucleation and development of a liquid phase within the syntactic foam, associated for example to the degradation of microsphere-matrix interfaces. This could explain the conductivity increase but a direct proportionality would be expected in this case. Another interpretation can be the leaching of alcalinous species from the microsphere glass [14] in hot wet conditions. This latter phenomenon surely contributes to the internal conductivity increase since there is no ionic ingress from external deionized water. Further work is in progress on this point.

## CONCLUSION

Impedance spectroscopy using a two electrode set-up is a multipurpose technique for studying epoxy/glass syntactic foam hydrolytic aging. The use of this technique to investigate composite coating performance should be enlarged.

The glass leaching was evidenced using ex situ measurements at room temperature on aged samples as well as in situ measurements during hot wet aging conditions. The conductivity increase presents a non trivial dependence on water uptake, building a master curve with different steps. Possible mechanisms accounting for the water uptake of syntactic foams during hydrolytic aging were identified and discussed.

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