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Romain Grangeat, Marion Girard, Cyril Lupi, Frédéric Jacquemin. Local water content field within an epoxy/metal bonded assembly in immersion. *The Journal of Adhesion*, 2023, 99 (3), pp.432-448. 10.1080/00218464.2021.2021893 . hal-04023811

**HAL Id: hal-04023811**

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Submitted on 30 Mar 2023

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# Local water content field within an epoxy/metal bonded assembly in immersion

R. Grangeat<sup>1</sup>, M. Girard<sup>1</sup>, C. Lupi<sup>2</sup>, F. Jacquemin<sup>1</sup>

<sup>1</sup>Institut de recherche en Génie Civil et Mécanique, GeM-E3M, UMR CNRS 6183, University of Nantes, France, 58 Rue Michel Ange 44600 Saint Nazaire

<sup>2</sup>Institut de recherche en Génie Civil et Mécanique, GeM-TRUST, UMR CNRS 6183, University of Nantes, France, 2 Chemin de la Houssinière 44300 Nantes

## Abstract

In this article a model of water diffusion within a bonded assembly will be set up. It will be fed by experimental tests which will allow to characterize the diffusive properties of a bonded assembly by taking into account the presence of interphases. For this purpose, specimens will be instrumented with Fresnel fiber optic sensors. These sensors allow a local measurement of the water content of a polymer material during wet ageing. Once these measurements are performed, the model, which will be called "gradient model", will then allow to calculate and represent the water content field at the core and at the interphases of an epoxy/metal bonded assembly. This model will be confronted with gravimetric tests in order to verify its good performance on the calculation of the global water content of an assembly.

## 1. Introduction

Currently, the technique of adhesive bonding has become indispensable in industry. It allows a better distribution of stresses, a reduction in weight, the assembly of different materials or even to allow additional functions such as sealing. However, one of the drawbacks of this assembly process is its durability through time, especially in wet conditions (humid air or immersion). As the adhesive is a polymer, hydrophilic by nature, water diffuses into it and affects its mechanical properties, resulting in the degradation of the global assembly properties [1]. When a bonded assembly is subjected to a humid environment, a change in the fracture surface can occur [2].

This was highlighted in the thesis work of Bordes [3], who showed the transition from cohesive failure (failure in the adhesive) to mixed failure (part of the failure occurs in the interface) after aging of a metal/metal bonded joint in sea water. This work presents the influence of water absorption in interfacial zone by focusing metal to metal bonded joints. This change in fracture surface is due to the diffusion of water that takes place in the interfacial zone. In a previous study [4], on the same material that is studied here, it was shown the effect of the interfacial zone on water diffusion. As known, when the adhesive is in a confined state between two substrates, the diffusion of water is more important and faster within this particular area, which could explain this change of failure faces during aging. The literature puts forward two hypotheses to explain this difference in kinetics within the interphases: the first is to take into account the effects of capillarity along the substrate [5][6] and the second is to consider an under-crosslinking of this zone which would accelerate water diffusion [7]. Capillarity is the phenomenon of physical interactions that can occur at the interface between water molecules and the substrate. In the work of Zanni-Deffarges and Shanahan [8], they consider that the adhesive/substrate interface can constitute a preferential route for water diffusion by capillary action. The second hypothesis is illustrated in the previous work [9] where the presence of a physico-chemical gradient is highlighted by in situ measurement with a fiber optic sensor. In this study, this gradient is assumed to be related to under-crosslinking. This is consistent with study of De Parscau du Plessix et al. [10] which showed a strong dependence of water diffusion kinetics on the cross-linking rate of an epoxy resin. Indeed, it is shown that water diffusion kinetics is faster and more important when the cross-linking of a material is lower. Whether it is the phenomenon of capillarity, or the under-crosslinking of the interphases, these two hypotheses are by no means contradictory. The difference in diffusive behavior between the interphases and the adhesive can result from both under-crosslinking and capillary action.

During water ageing, the interfacial zone is the weak point of bonded assemblies. As known, the diffusion of water is faster and more important.

From a diffusive point of view, interphases have already been macroscopically characterized using an analytical model [4]. However, this model does not allow estimating the local behavior of the water content, so it is not possible to predict the mechanical long-term behavior of a bonded assembly. The aim of this work is to establish an efficient and relevant model to determine the local moisture content field of a bonded assembly. To feed this model, local measurements of water content will be performed using a fiber optic sensor in the core and in the interfacial zone of the assembly. First, the scientific approach followed will be explained.

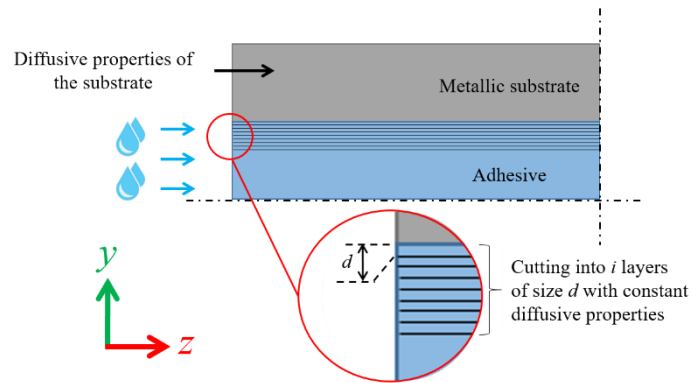
## 2. Scientific approach

The objective of this study is to be able to represent the local water content field within a bonded assembly by taking into account the presence of interphases. These interphases are formed during the cross-linking of the adhesive by reacting locally with the substrates and lead to the presence of a physicochemical property gradient, normal to the substrate, through the thickness of the adhesive joint [9] [11]. Diffusive parameters being dependent on physicochemical properties [10], the interphases cause a gradient of diffusive properties (diffusion coefficient and water content at saturation). Estimation of the local water content field then involves modelling water diffusion in the assembly and identifying this gradient of diffusive parameters. The consistency of the approach and the hypotheses can then be verified by comparing the numerical results with other series of macroscopic experimental measurements.

### 2.1 Modelisation of water diffusion in the assembly

Considering that the surface subject to environmental conditions is the free surface of the adhesive, and that the dimension  $x$  is infinitely large in front of the two others (see **Fig. 1**). It is therefore possible to consider, at first order, that the diffusion is mainly unidirectional following

the  $z$  direction, perpendicular to the properties gradients. To represent it, the interphase will be considered as a succession of fine layers of thickness  $d$  with constant diffusive properties, in which the water diffuses unidirectional following  $z$ .



**Fig. 1.** Schematic diagram of a quarter specimen of a bonded joint

Each layer has its own diffusive properties resulting from the formation of interphases and the resulting physico-chemical gradient.

It is assumed that the same diffusion model could be applied throughout the whole thickness of the bonded assembly, only the diffusive parameters will be different. Previously, tests have been made on the bulk adhesive. The diffusion model used in bonded assembly will therefore be the one identified on the adhesive alone.

## 2.2 Identification of gradient of diffusive parameters

The physicochemical gradient in the interphase was characterized for a given assembly in a previous study (commercial epoxy adhesive / stainless steel substrate) [9]. The object of this work here is therefore to make the link between the diffusive property gradient and the physico-chemical property gradient in the dry state, before ageing, in the same assembly, based on local experimental measurements of water content and a few hypotheses.

In this work two other strong hypotheses will be made: The first one is that the influence of the physico-chemical gradient on water diffusion kinetics is mainly due to the under-crosslinking

gradient, and the second one is that capillary effects will be neglected. In this way, it is possible to use a direct link between the sub-crosslinked material and its diffusive properties, highlighted in a previous study [8].

In order to identify these parameters, in situ measurements using the Fresnel sensor, will be carried out. This sensor allows the measurement of the local water content. By positioning sensors at different distances from the substrate, it will be possible to make a local measurement of the water content for different layers. Once this measurement is performed, the diffusion parameters will be identified for the measured layers. A gradient model will then be set up to plot the evolution of the diffusion parameters as a function of the thickness of the bonded joint, based on physicochemical gradient measured.

Once these diffusive parameters have been determined, the local water content field in the entire adhesive joint can be calculated taking into account the interphases.

### 2.3 Experimental validation

Once the model is set up, it will be possible to represent the water content field of the bonded assembly. By integrating the water content field over the volume of the assembly, it is possible to calculate the global water content. This global water content can be measured experimentally using gravimetric tests which consist in following the mass of a specimen over time. Gravimetric tests on non-instrumented specimens of different thicknesses will therefore be carried out to validate the gradient model. These tests will allow to trace the macroscopic water setting kinetics of different thickness assemblies. These results will then be compared to those obtained from the gradient model. It will then be possible to conclude on the performance of this model and the validity of the assumptions.

### 3. Materials and methods

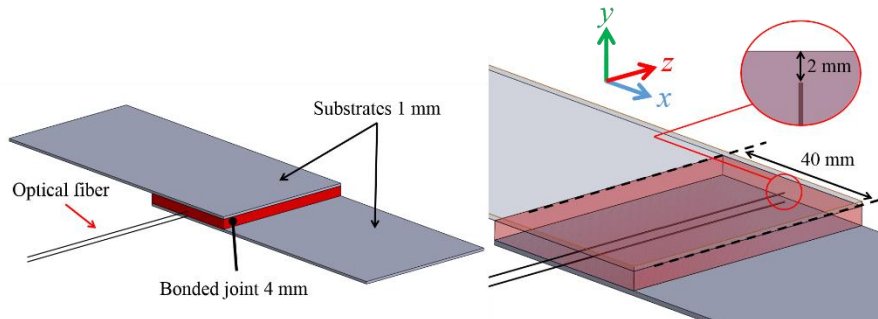
#### 3.1. Bonded assemblies

The material of this study is a commercial two-component epoxy adhesive. The application process was set at 24 hours under ambient conditions followed by a 24 hours post-curing at 60 °C. This application process was set to obtain a stable and fully cross-linked material. Metal-to-metal connections were made with 316L stainless steel substrates. These substrates were previously sandblasted to increase roughness and remove the native oxide on the surface. The grit used is “Corrinbon brun 150” which corresponds to aluminum oxide. Attention is paid to the parameters used to ensure reproducibility for the different tests. A careful degreasing with methylethylketone (MEK) was then performed.

#### 3.2. Fiber optic measurements

Optical fiber is a waveguide with the ability to conduct light. It generally consists of two concentric silica cylinders: the optical core and the optical cladding. The optical fibers used in this study are single-mode fibers (SMF28). In this study, two sizes of optical fibers will be used, one with a 125  $\mu\text{m}$  optical cladding (produced by iXblue IXF-SM-1550-125) and one with an 80  $\mu\text{m}$  optical cladding (iXblue IXF-SM-1550-80). In both cases, the optical core is 8  $\mu\text{m}$ . All measurements will be performed using a laser with a wavelength of 1550 nm. By cleaving the end of an optical fiber it is possible to create a diopter. Following the laws of Snell-Descartes [12], a portion of the incident wave is reflected by the diopter. By measuring the optical power of this reflection, it is possible to determine the refractive index of the environment where the diopter is positioned (cleaved end of the fiber) [13]. This sensor, called a Fresnel sensor, allows to measure locally the index of refraction of a material, the measurement being carried out at the end of the optical fiber. It was shown in a previous study the possibility of measuring the local water content without calibration in an adhesive epoxy [14]. For this purpose, a model was used to relate the local refractive index to the local water content. Still with the aim of

locally measuring the water content within the interfacial zone, bonded assemblies will be instrumented (Fig. 2).



**Fig. 2.** Instrumentation of a bonded assembly

Substrates with dimensions of 60 x 120 mm<sup>2</sup> with a 4 mm thick bonded joint and a 40 mm overlap were used. The sensors are positioned at four different distances from the substrate: 40  $\mu\text{m}$ , 62.5  $\mu\text{m}$ , 125  $\mu\text{m}$  and 2000  $\mu\text{m}$ . Two specimens were instrumented by three sensors (number of interrogation systems that we have at this time). It was possible to realize two measuring points for the distances of 40  $\mu\text{m}$  and 2000  $\mu\text{m}$  and one measuring point for 62.5  $\mu\text{m}$  and 125  $\mu\text{m}$ .

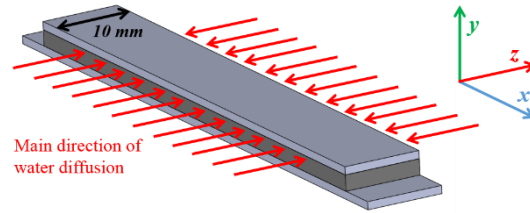
The sensor insertion process is the same as in a previous study [9]. The sensors have been previously bonded on the substrate with epoxy bond point, the interrogation distance to the substrate is controlled by the diameter of the optical fibers used (Fig. 4-b). After the measurements, analyses were performed to verify the position of the sensors. The instrumented assemblies were then be aged in distilled water at 40 °C. During the ageing process, the refractive index evolution will be measured for the different positions of the sensors.

### 3.3. Gravimetric measurements

As highlighted in the scientific approach part of the project, gravimetric tests on non-instrumented specimens will be carried out in order to verify the good performance of the model



that will be set up. The geometry chosen is the following, it allows to consider a diffusion mainly according to  $z$ .



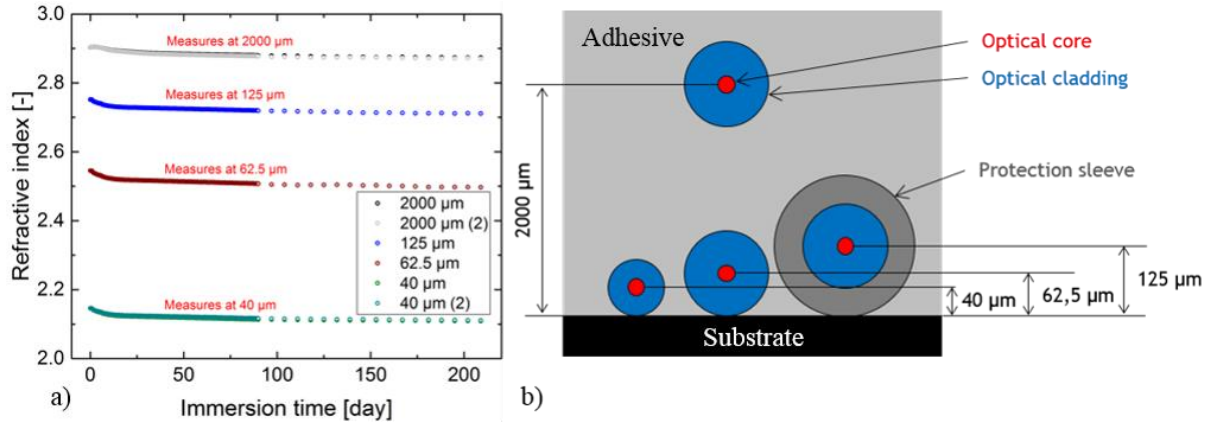
**Fig. 3.** Bonded assemblies for gravimetric tests

It was decided to make assemblies of several thicknesses: 1, 2 and 5 mm in order to check the good holding of the model for different assemblies. The results obtained have been published previously. In this previous study [4], the water diffusion kinetics of the bulk adhesive was determined using gravimetric tests. A diffusion model was used to identify the diffusion parameters. These parameters will be used in the following of this article.

## 4. Results and discussions

### 4.1 Optical characterization of the interphase during water diffusion

The two instrumented specimens with three sensors each were immersed at 40 °C. The refractive index was continuously monitored during the first three months of immersion and for the last three months punctual measurements have been carried out every 10 days (Fig. 4-a).



**Fig. 4.** a) Refractive index evolution as a function of immersion time for different distances from the substrate; b) Diagram of the position of the sensors in the bonded assembly, the optical core represents the interrogation surface of the sensors

Before ageing, the refractive index depends on the distance from the substrate. This result was discussed in a previous study [9], the refractive index of the bonded assembly was measured at different distance from the substrate. He has showed that this property gradient comes to interphase's presence. During the ageing, the results of the Fig. 4 show a drop in refractive index and can be related to the local water content.

## 4.2 Characterization of the local water content of the interphase

In order to estimate the local water content using refractive index measurements, it was considered that the evolution of the index in the interphase is identical to the evolution in the assembly in relation to the water content.

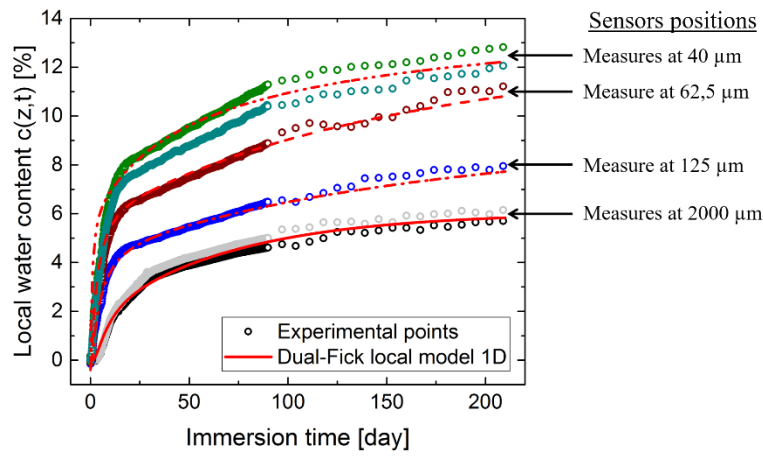
The Maxwell-Garnett model was used to relate the optical index of a polymer material to its water content.

This model was discussed in the following article [14] and is recalled below:

$$n_{a/w}(t) = n_a \sqrt{\frac{1 + 2f(t) \frac{n_w^2 - n_a^2}{n_w^2 + 2n_a^2}}{1 - f(t) \frac{n_w^2 - n_a^2}{n_w^2 + 2n_a^2}}} \quad (1)$$

With  $n_{a/w}(t)$  the refractive index of the adhesive/water system which depends on the immersion time,  $n_a$  the refractive index of the adhesive ( $n_a = 2.904$ ),  $n_w$  the refractive index of the water ( $n_w = 1.333$ ) and  $f(t)$  the volume fraction of water.

Using the previous results of the Fig. 4 and the Maxwell-Garnett model, it is possible to determine the evolution of the local water content for different positions in the assembly. These results are illustrated Fig. 5.



**Fig. 5.** Evolution of local water content as a function of immersion time for different distances from the substrate. The results show different water diffusion kinetics depending on the position in relation to the substrate. Close to the substrate, the faster the water diffusion kinetics and the higher the water content. To identify these results, the local Dual-Fick diffusion model was used [15] (2).

$$c(z, t) = \sum_{i=1}^2 \left[ C_{si} \left( 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \exp \left[ -(2n+1)^2 \pi^2 \cdot \frac{D_i \cdot t}{e^2} \right] \cos \left[ (2n+1) \pi \frac{z}{e} \right] \right) \right] \quad (2)$$

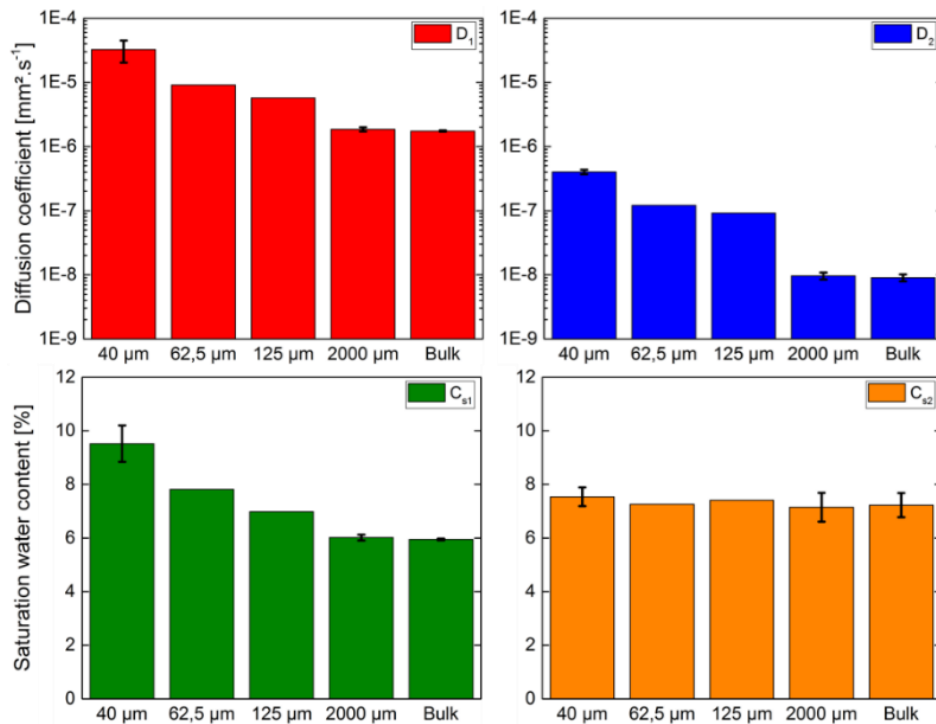
As know, it is with this model that the diffusion parameters of the bulk adhesive were identified in a previous study [4]. Considering a 1D diffusion, it is possible to use the local solution of the Dual-Fick model to identify diffusion parameters [15] (2) ( $D_1$ ,  $D_2$ ,  $C_{s1}$  and  $C_{s2}$ ). Tab. 1 summarizes the various diffusion parameters that have been identified and that make it possible to draw the red dotted curves of Fig. 5. The parameters obtained are compared with those

determined on a bulk specimen. Gravimetric tests were performed on bulk under the same ageing conditions as the bonded assemblies.

Parameters	Bulk adhesive [4]	$d = 2000 \mu\text{m}$	$d = 125 \mu\text{m}$	$d = 62,5 \mu\text{m}$	$d = 40 \mu\text{m}$
$D_1$ (mm <sup>2</sup> /s)	$(1,74 \pm 0,04) \cdot 10^{-6}$	$(1,86 \pm 0,14) \cdot 10^{-6}$	$5,72 \cdot 10^{-6}$	$9,08 \cdot 10^{-6}$	$(3,25 \pm 1,22) \cdot 10^{-5}$
$D_2$ (mm <sup>2</sup> /s)	$(9,01 \pm 1,10) \cdot 10^{-9}$	$(9,65 \pm 1,18) \cdot 10^{-9}$	$9,17 \cdot 10^{-8}$	$1,21 \cdot 10^{-7}$	$(4,01 \pm 0,32) \cdot 10^{-7}$
$C_{s1}$ (%)	$5,95 \pm 0,03$	$6,02 \pm 0,11$	6,98	7,82	$9,52 \pm 0,68$
$C_{s2}$ (%)	$7,23 \pm 0,45$	$7,15 \pm 0,54$	7,41	7,26	$7,54 \pm 0,35$

**Tab. 1.** Diffusion parameters determined for different distances from the substrate, comparison with parameters identified on the bulk adhesive

It is possible to compare the different parameters identified in relation to the distance to the substrate (Fig. 6).



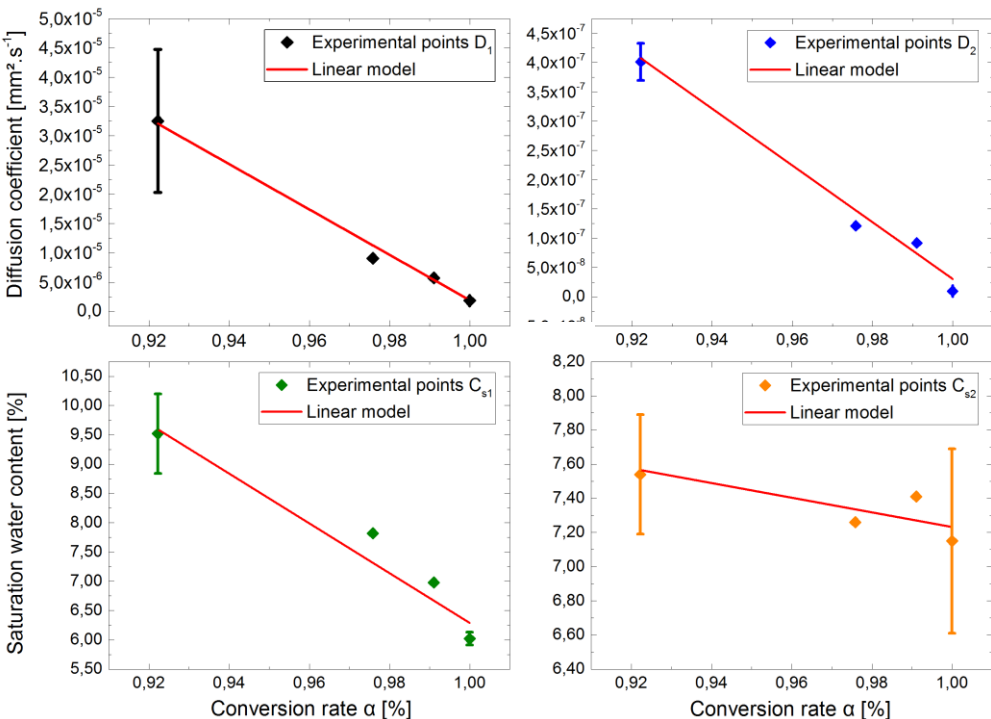
**Fig. 6.** Comparison of diffusion parameters with respect to distance from substrate and bulk adhesive

The parameters therefore depend on the distance  $d$  from the substrate. At 2000  $\mu\text{m}$ , i.e. at the core of the assembly, the identified parameters are equivalent on a bulk adhesive specimen. Water diffusion at the core of the assembly is therefore identical to that observed on the bulk adhesive. The Fig. 6 also shows different water diffusion kinetics in the interfacial zone. Indeed, the diffusion coefficients  $D_1$  and  $D_2$ , and the saturation water content  $C_{s1}$  are higher close to the

substrate. Concerning the parameter  $C_{s2}$ , it seems constant whatever the distance from the substrate. This result should be put into perspective since saturation has not been reached, the identification made is not complete and cannot be extrapolated for longer ageing times. These results provide initial information on the gradient of diffusive properties of the interphases but do not allow to fully characterizing it. This is the subject of the next part.

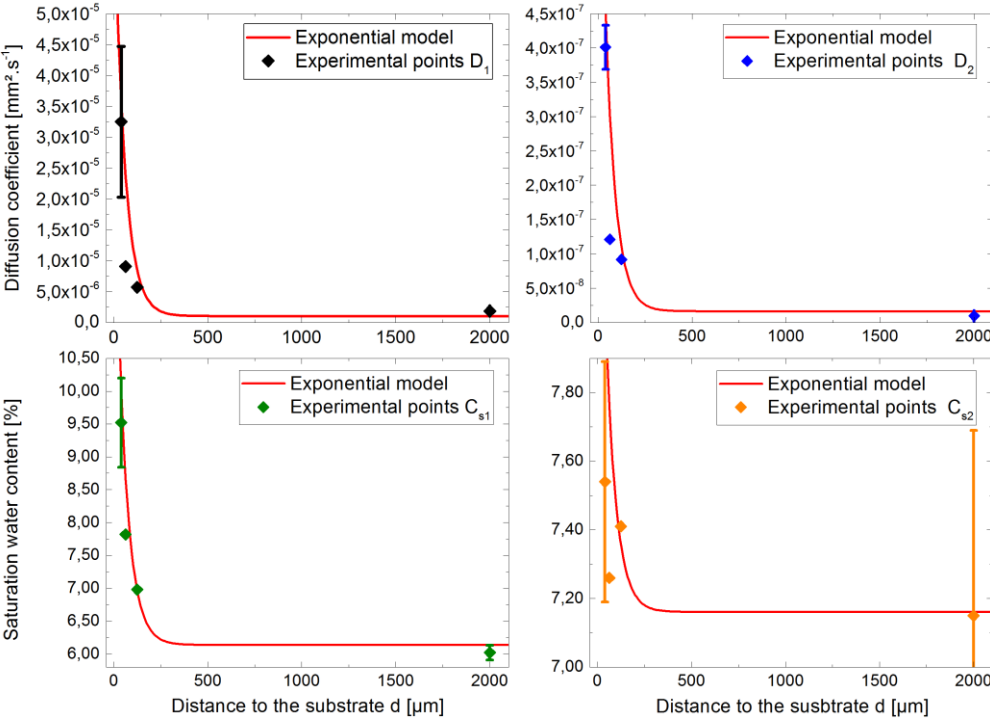
### 4.3 Gradient of diffusive properties within the bonded joint

The undercross-linking of the interphase is one of the hypotheses that can explain why the diffusion of water is more important and faster in this area. In a previous study, measurements were made to measure the conversion rate of the adhesive in the interphases of a bonded assembly [9]. These measurements were performed at the same distance as those performed in this article. The diffusive properties can therefore be related to the conversion rate, this result is illustrated in Fig. 7.



**Fig. 7.** Evolution of the diffusive parameters as a function of the conversion rate of the adhesive, use of a linear approximation

In their work, De Parscau du Plessix et al. [10] modelled the relationship between diffusive parameters and the conversion rate of an epoxy resin, their results show a linear relationship. A linear approximation was then used between the diffusive parameters and the conversion rate of the adhesive (Fig. 7). This approximation shows a drop in diffusive properties relative to the conversion rate. An exponential model was used in order to represent the evolution of the conversion rate in relation to the distance from the substrate [9]. Using this exponential model and the linear approximations of Fig. 7, the diffusive properties can be estimated in relation to the distance from the substrate.



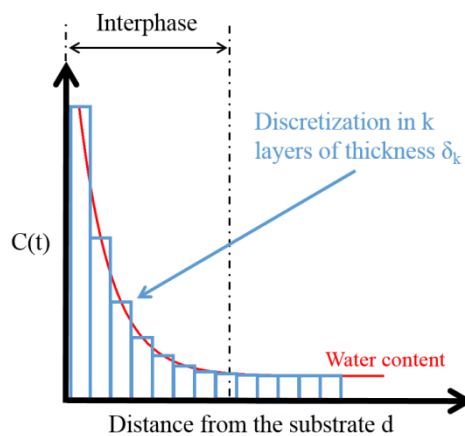
**Fig. 8.** Evolution of diffusive parameters as a function of distance from the substrate, use of the exponential model used to relate the conversion rate to the distance from the substrate

The results of the Fig. 8 allow to represent the gradient of diffusive properties present within a bonded joint, and thus to fully characterize in the thickness of the adhesive joint the diffusive properties. It is important to note a high standard deviation for the  $C_{s2}$  parameter. This high standard deviation comes from the fact that we did not reach water saturation during the ageing

of the bonded assemblies. Now, to determine the water content field a model will be set-up using the previous characterization.

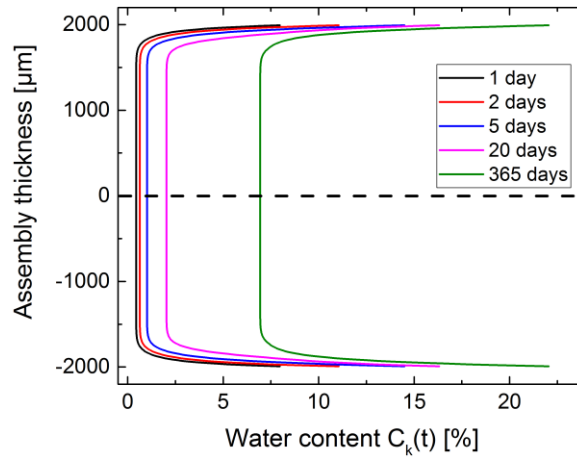
#### 4.4 Gradient model to determine the water local content field within the bonded assembly

In this part, a model, called gradient model, will be set-up. Experimental results on local water content measurements show a gradient as a function of distance from the substrate (Fig. 5). To calculate the water content field present in a bonded assembly, the thickness of the assembly is then discretized into  $k$  layers of thickness  $\delta k$  where the global water content is considered constant at a given time (Fig. 9).



**Fig. 9.** Modeling of the global water content of each layer within a bonded assembly by discretizing the thickness of the assembly in  $k$  layers  $\delta k$  at a given point in time

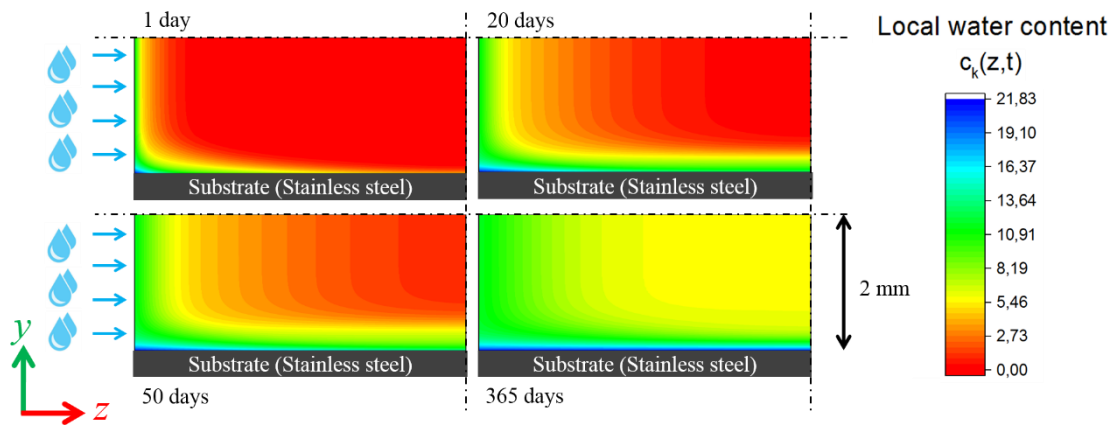
In the following, the global water content of each layer will then be noted  $C_k$ . To calculate it, the idea is to consider an independent unidirectional diffusion in each layer with a Dual-Fick model. The diffusive parameters of the model are computed for each layer by averaging the results obtained in the previous section (Fig. 8), identified according to the distance to the substrate. The thickness of each layer is fixed at  $8 \mu\text{m}$ , it corresponds to the interrogation size of the Fresnel sensor. The application of the global solutions of the Dual-Fick model allows to calculate and plot the evolution of the global water content of each layer at a given time (Fig. 10). Calculations are indicative for times ranging to 365 days.



**Fig. 10.** Representation of the global water content in each layer in the thickness of an assembly calculated using the gradient model

The results show a higher global water content for the layers in the interphases. Indeed, after one year the water content is almost four times higher than at the core of the assembly. By considering diffusion according to the variable  $z$ , it is possible to represent the local water content field  $c_k(z, t)$  of each layer for different distances from the surface in contact with water. For this purpose, the local analytical solution of the Dual-Fick model was used at a given time  $t$ . This solution represents the local water content as a function of space and time. Calculations were performed within a 2 mm thick and 10 mm long bonded assembly. With this calculation to reach saturation it would be necessary to carry out a simulation over more than 70 years. This is due to the size of the specimens. The implemented gradient model considers a unidirectional diffusion according to  $z$ . For extremely long periods of time, the water molecules will tend to diffuse also towards the center of the specimen, i.e. in the transverse  $y$  direction. A 2D diffusion model should therefore be set up. In this context, it was decided to extrapolate the results only over one year of immersion. Since the problem is considered symmetrical, only a quarter specimen is shown on the Fig. 11.

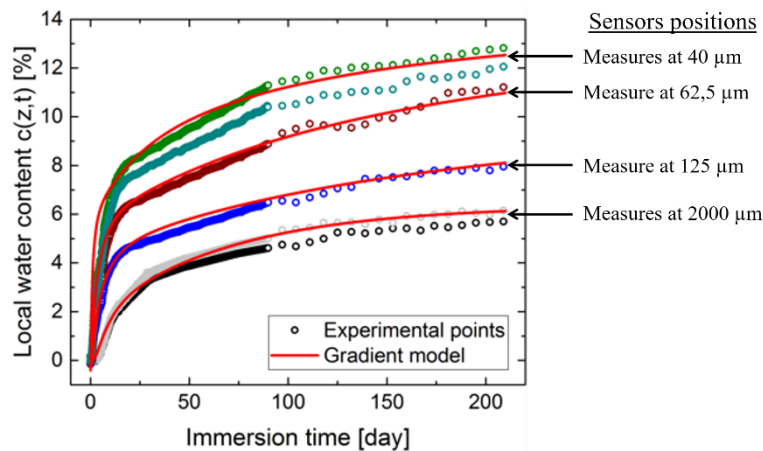




**Fig. 11.** Local water content field  $c_k(z,t)$  in a quarter specimen calculated in each  $k$  layer of the gradient model with the local analytical solution of the Dual-Fick model

The water content field plotted with this model is used to represent the water diffusion front within a bonded assembly. In addition to higher water content, the kinetics is faster in the interphase. The water diffusion front is not homogeneous in thickness. These results are in line with the hypotheses put forward in the thesis of Bruneaux [16] regarding the appearance of the water content field in a bonded assembly.

With this model, it is possible to calculate the local water content at sensors that have been positioned at different distances from the substrate. These results have been compared with the experimental measurements performed previously (Fig. 5).

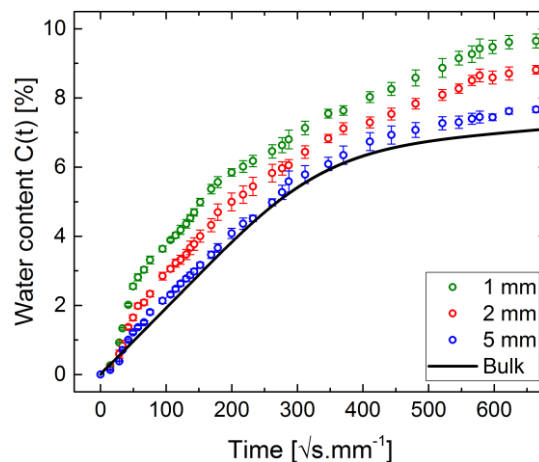


**Fig. 12.** Comparison between the local water content calculated with the gradient model and experimentally measured with fiber optic sensors at different distance from the substrate

The model implemented allows to reliably represent the local water content measurements carried out. It is therefore possible with this model to represent the local water content field within a bonded assembly taking into account the interphases. In the following, the model will try to be validated by calculating then comparing with gravimetric tests the global water content of a bonded assembly.

#### 4.5 Model validation: comparison of global water content measurement with gravimetric tests and calculation with the gradient model

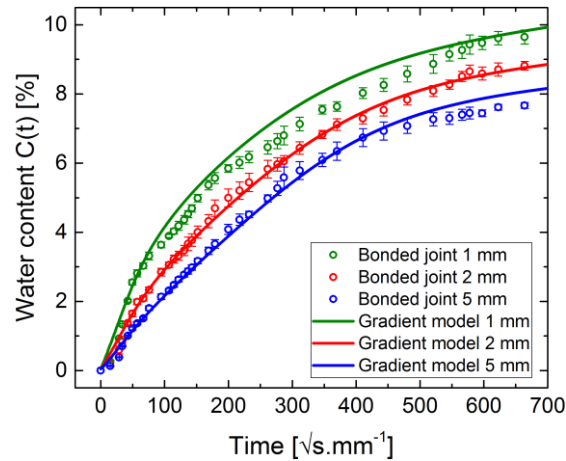
To validate the gradient model, the analytical results obtained will be compared with gravimetric tests obtained in the previous study [4] on three different thicknesses of bonded assemblies : 1, 2 and 5 mm (Fig. 13).



**Fig. 13.** Evolution of the macroscopic water content as a function of immersion time for different bonded joint thickness

The results show a dependence of the water diffusion kinetics on the thickness of the bonded joint. Indeed, for a thin bonded joint (1 mm) the specimen absorbs a larger quantity of water with a faster diffusion rate than the kinetics observed on bulk adhesive. For a significant thickness (5 mm) the observed kinetics seem to follow that of bulk. These results can be attributed to the presence of interphase in the bonded joint. Indeed, in the case of thin adhesive thicknesses, the interphase has a higher proportion than in the case of thicker thicknesses. Finally, these results highlight the impact of interphases on water diffusion kinetics. By

integrating on the volume the water content fields obtained previously with the model set up (Fig. 11) for different immersion times and different joint thicknesses, it is possible to represent the macroscopic water content. This result can be compared with the gravimetric tests (Fig. 14).



**Fig. 14.** Evolution of the macroscopic water content within assemblies of different thicknesses. Comparison between the gradient model and the gravimetric tests

In conclusion, this model allows a relatively good representation of the macroscopic results obtained during the gravimetric tests. What is all the more encouraging is that these two sets of results are totally independent. The largest discrepancy between the experimental data and the modelling concerns the thinnest assemblies (1 mm thick). The average deviation from the gradient model is 3.9 %.

## 5. Conclusion

The methodology used in this work highlighted the possibility of characterizing the diffusive properties of the interphases of a metal/epoxy assembly. For that, a gradient model has been set up. In a first step, fiber optic sensors based on Fresnel reflection were positioned within a bonded assembly at different distances from the substrate in order to interrogate the interphase. Experimental measurements allowed, using an optical model, to estimate the local water content for the different positions. For a given position, it is then possible to determine the diffusive parameters. By interpolating the results obtained, the diffusive characteristics of the interphases

were characterized. Once these parameters were estimated, a gradient model was set up and allowed to represent the water content field within a bonded assembly. To verify the correctness of this approach, the water content field was integrated to go back to the macroscopic water content. This water content was then compared with results obtained using gravimetric tests. The diffusive parameters used for the interphases allow a relatively good representation of the water contents measured by the gravimetric tests. It was found that there was a higher water uptake within the interphases. This result explains the change in failure facies classically observed during the ageing of a bonded assembly [2]. The water molecules will tend to degrade the interfacial zone. This degradation leads to a change from cohesive to adhesive failure.

## Acknowledgement

This study is part of the INDUSCOL project and the authors wish to associate the industrial partner of this project; Naval Group. This work benefited from France Energies Marines and State financing managed by the National Research Agency under the Investments for the Future program bearing the reference ANR-10-IED-0006-08.



ANR-10-IED-0006-08

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