Method of characterizing the interphase's mean water diffusion properties of a bonded assembly in immersion

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Abstract

The durability of bonded structures in wet environments is the subject of a large number of studies. The long-term behavior of these structures is affected and driven by the water diffusion within the adhesive. The literature highlights that the creation of interphases, particular area where chemical and physical bonds are established between the adhesive and the substrate, play an important role in water diffusion kinetics [1].

The aim of this study is to provide a method to characterize the mean water diffusive properties of the interphases of a bonded assembly in immersion. This approach includes global gravimetric tests of an assembly and an analytical model to characterize its water diffusive parameters. The model divides the bonded joint into two separate layers: one layer representing the adhesive and the other the interfacial area. The water content of each layer can then be estimated using analytical equations. Diffusion parameters are then deduced from these water contents. A greater and faster water diffusion within the interfacial zone has been highlighted. The approach presented here allows to quantify it.

Keywords: adhesive bonding, interphase, durability, water diffusion, characterization

1. Introduction

In recent years, the use of bonded assembly has increased in industry in all sectors, including aerospace, marine, automotive and many others [2-3]. The bonding technique competes with other assembly processes such as welding, riveting or screwing. In the case of welding, the local increase of temperature leads to residual stresses and microstructural changes. With regard to riveting or screwing, these methods consist in to put in place rivets or screws. Drilling is then necessary in both cases and leads to local stress. These three assembly techniques, can play a negative role on the durability of the structure. Indeed, stress localization is often at the origin of cracking of one or both of the assembled materials. In contrast to these processes, bonding allows for a homogeneous distribution of stresses. Since the bonding surface is often much larger than that created by a mechanical assembly, the stresses applied are lower and the assembly is less sensitive to the failure. In addition, bonding offers the possibility of assembling materials of different natures [4].

Nevertheless, despite of the many possibilities and advantages mentioned above, there is still some doubt to bonded assembly technology. One of the reasons is the lack of information concerning the durability of the assembly over time, especially in wet environment. Indeed, adhesive is a polymer, which is therefore hydrophilic nature by definition. Much more than other assembly techniques, bonding is strongly influenced by the surrounding environment, especially when it is in wet condition [5]. The diffusion of water has a significant impact on the mechanical properties like glass transition temperature, elastic modulus and rupture strength [6]–[8]. Estimating the strength and durability of bonded joints in a wet environment is then a key issue for some applications.

A first approach consists in estimating the diffusive properties of the adhesive on a bulk sample, and to couple the water diffusion with the degradation of the mechanical properties. However in the literature, Zanni-Deffarges [1] observed faster water diffusion when the adhesive is within a bonded assembly. They explained this difference in kinetics by the presence of interphases. Bikerman [9] is the first to postulate the hypothesis of an interphase between two materials. It is a transition area between the substrate and the adhesive with gradients of structures and properties. The nature and size of the interphases are dependent on substrates and adhesive nature [10]. In following, study will be limited to metal substrates with epoxy type structural adhesives. In literature, interphase thickness has been identified between some tens and some hundred microns and depends on the nature of the substrate, the surface preparation and the adhesive properties [11-12]. During the diffusion of water, Chan [13] and O'Brien [14] have shown an accumulation of water molecules in the interphases using infrared spectroscopy measurement. These different results show the complexity of the phenomenon of water diffusion in a bonded joint.

To explain these phenomena, there are two hypotheses detailed in the following: the first one consists in taking into account the capillary effects along the substrate and the second in considering an under-crosslinking of this area that would accelerate water diffusion. Capillarity is the phenomenon of physical interactions that can occur at the interface between water molecules and the metal substrate. In their work, Zanni-Deffarges [15] consider that the adhesive/substrate interface can constitute a preferential way for water diffusion by capillary effects. They explain this phenomenon by the surface energy of the substrates being high enough for water/substrate interactions to form instead of adhesive/substrate interactions. The literature shows that the capillary phenomenon can be amplified when the substrate surface has hydrophilic polar sites [14-15]. The second hypothesis is an under crosslinking of the interphases. Indeed, it was revealed, in a previous study [12], the presence of this under

crosslinking at the interface between the adhesive and the substrate used in this study. However, De Parscau du Plessix et al. [18] showed a dependence of the water diffusion kinetics on the crosslinking rate of an epoxy resin. He showed that water diffusion is faster when the conversion rate is lower. When a material is not fully crosslinked, its molecular weight is lower, resulting in a lower density. This will make it easier for water molecules to be absorbed and diffuse within the material. This hypothesis also helps to explain what has already been observed, that is a higher water content in the interphases [13][14][19]. These two hypotheses are not contradictory. The difference in diffusive behavior between the interphases and the adhesive can result from both under crosslinking and capillarity.

In conclusion, the literature shows that water diffusion is faster in bonded joint than in the bulk adhesive, in particular due to interphases presence. Water diffusion kinetics are therefore different in these two conditions. However, the too few of local results available also show how difficult it is to quantify this kinetics, which can become problematic when estimating the lifetime of a bonded structure. The question to which this study tries to provide elements of answer is a quantification of the water diffusion kinetics in bonded assemblies and more particularly in interphases.

It is proposed here an experimental method, based on classical gravimetric monitoring, coupled to an analytic model allowing to quantify the mean diffusive parameters of the interphase layer and the rest of the adhesive in a direct way.

The plan of this work is divided into 3 parts: in the first one, the starting hypothesis and the scientific approach (experimental and analytical model) are explained, in the second one, the experimental protocol is detailed. Finally, in the third part, the experimental results are presented along with their exploitation, in particular with the help of the analytical model set

up. This exploitation leads to the characterization of the mean diffusive parameters of the interphase layer.

2. Scientific approach

2.1 Revealing of the interphase influence on the water uptake of bonded joint during humid ageing

The starting hypothesis formulated here is that the interphase between a metal substrate and an epoxy adhesive is identical in nature and thickness, and does not depend on the total thickness of the bonded assembly. This statement is reasonable when the thickness of the bonded joint is large front the thickness interphase. The principle of a joint of at least four time as much of the interphase will be maintained. When the bonded assembly is placed in a wet environment, there will be a contribution from the interphase and a contribution from the original adhesive part on the mass change attributed to water absorption. If the thickness of the bonded joint changes, the interphase contribution then will not depend on the thickness of the bonded joint.

To formalize things, from a macroscopic point of view, we can consider a bonded joint, of thickness *et*, represented by two layers of different natures: one interphase layer (repeated twice on each substrate) of thickness *ei* with average diffusive properties, and another, the original adhesive layer, of thickness *eb*, also with average properties (Figure 1). If this hypothesis is verified, then considering different sample noted j of different thicknesses et_j (with $et_j > 4.ei_j$ and j number of sample), the contribution of the interphase layer on the water uptake should remain the same while the contribution of the original adhesive layer should be proportional to the thickness eb_j. The first idea is then to make adhesive bonding samples of three different thicknesses ($et_1 < et_2 < et_3$) and to follow their evolution in mass during water diffusion. A different weight variation will then show us the importance of the influence of the interphases.

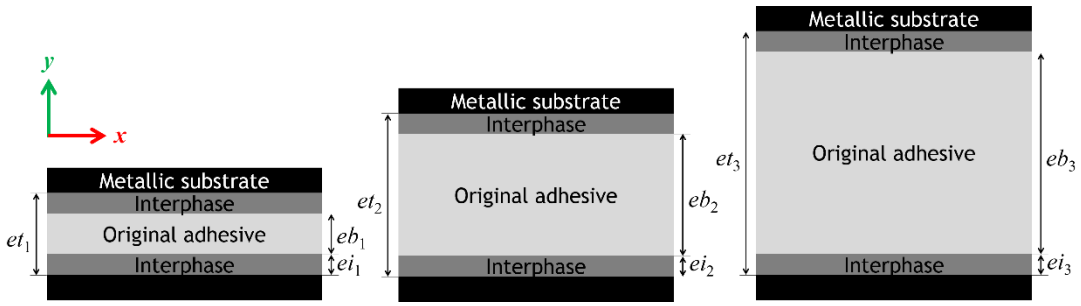

Figure 1. Schematic diagram of a bonded assembly with interphases for three different thicknesses of bonded assemblies

As mentioned above, note that the thickness of the interphases is considered identical whatever the sample j.

2.2 Toward the quantification of the water uptake of the interphase layer of a bonded assembly in a wet environment

The water uptake of the interphases must be quantified when it is sufficiently large in relation of the rest of the bonded assembly. This quantification makes it possible to give elements of response with regard to the service life of a bonded structure in a wet environment. An analytical model will be set up in order to characterize the mean diffusive parameters of the interphase layer using only the gravimetric results.

As presented above, the main idea here is that the contribution of the interphase and the original adhesive can be dissociated on the total water uptake. For every time step *t*, while the interphase water uptake over time, noted *Δmi(t)*, remains constant for all samples, the water uptake in the original adhesive, noted *Δmb(t)*, should be proportional to its thickness *eb*. For each sample j and whatever $t > 0$, we can then write that its total water uptake $\Delta mt_j(t)$ follows the equation (1).

$$\Delta mt_j(t) = \Delta mi(t) + \Delta mb_j(t) = \Delta mi(t) + \Delta\overline{mb_j}(t).eb_j \qquad (1)$$

where $\Delta mt_j(t)$, $\Delta m_i(t)$, $\Delta mb_j(t)$, $\Delta\overline{mb_j}(t)$ and eb_j are respectively the total mass uptake of bonded assembly due to water, the mass uptake of interphase layer, the mass uptake of original adhesive layer and the mass uptake of original adhesive normed by its thickness eb_j.

The equation (1) represents an affine relationship between the mass uptake of the bonded assembly and the thickness of the original adhesive layer: the slope is $\Delta\overline{mb_j}$ and the intercept represents Δmi (Figure 2).

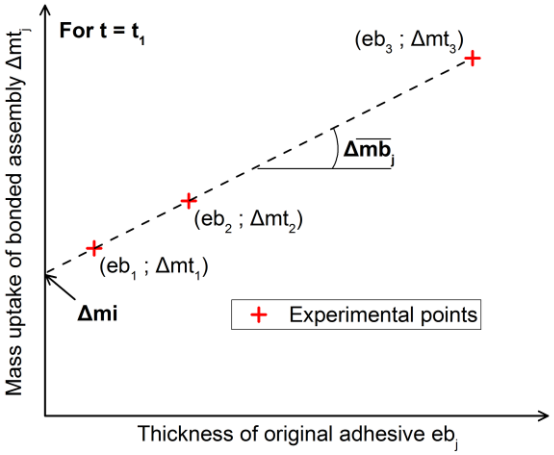

Figure 2. Principle graph of the evolution of the mass of an assembly as a function of the thickness of the original adhesive layer

2.3 The dual layer model: assumptions and quantification of water uptake

The measurement of the mass variation of several bonded assembly samples of different thickness would then make it possible to quantify the specific mass setting of the interphase over time. To characterize the diffusive properties of the interphase, it is necessary to relate this mass variation to a water content in the interphase. The following hypothesis are proposed in this model (those already stated above are repeated here):

- In view of the symmetry of the problem, only half of the joint will be studied;

- Division of the bonded joint half into two layers of constant thickness *ei* and *eb*/2, with average properties and uniform in thickness;

- The thickness of each layer is considered constant during ageing (neglected swelling and no interphase growth);

- The thickness of the interphase is constant whatever the thickness of the joint;

- Water diffusion is considered unidirectional in direction *x* (on scheme Figure 1). In this case, the water content in each layer can be considered constant in thickness and the water front in each layer is perpendicular to direction *x*.

The objective here is to analytically dissociate the macroscopic water content in the interphase layer *Ci(t)* and in the original adhesive layer *Cb(t)* over time. From equation (1) and by working on the standard water content in relation to the thickness of each layer, it is possible to write the analytical expression describing the total water mass of a bonded joint as a function of the water mass included in each layer (2). This equation is available whatever $t > 0$.

$$\Delta\overline{mt_j}(t)et_j = \Delta\overline{mi}(t)2ei + \Delta\overline{mb_j}(t)(et_j - 2ei) \quad (2)$$

Where $\Delta\overline{mt_j}$, $\Delta\overline{m_i}$ and $\Delta\overline{mb_j}$ respectively represent the normalized water mass of the assembly, the interphase layer and the original adhesive layer.

By considering equivalent densities between the interphase part and the original adhesive part it is possible to calculate the water content of the assembly $C_j(t)$ (3) whatever $t > 0$.

$$C_j(t) = Cb_j(t) + \frac{2ei}{et_j}(Ci(t) - Cb_j(t)) \quad (3)$$

where $C_j(t)$, $Ci(t)$ and $Cb_j(t)$ respectively represent the water contents of the assembly, the interphase layer and the original adhesive layer.

The equation (3) represents the evolution of the macroscopic water content of the assembly as a function of the thickness of the bonded joint et_j and is illustrated in Figure 3 for a given time step.

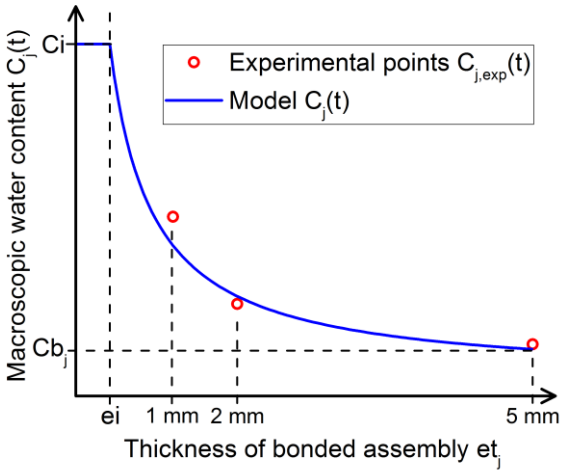

Figure 3. Evolution of the water content of the bonded joint as a function of the thickness of the bonded joint at a given time *t*

In order to determine the macroscopic water contents in the interphase layer *Ci*(t) and in the original adhesive layer *Cb(t)*, it is necessary to adjust the function $C_j(t)$ of the equation (3) with experimental points (red points on the Figure 3). These points will be noted $C_{j,exp}(t)$, and will be measured with gravimetric tests for each bonded joint thickness et_j and for each measurement time. These tests will allow us to determine water diffusion kinetics (water content as a function of time), will used to quantify the diffusive parameters of the interphases. The experimental protocol is explained in the following section.

3. Materials and methods

3.1 Sample geometry

In this study an epoxy adhesive was used. The objective is to determine the water diffusion kinetics in the case of bonded assembly. In this context, parallelepiped specimens with three

different thicknesses e_j have been manufactured as described in Figure 1. Given the size of the classically observed interphases (a few hundred micron), we decided to work on 1, 2 and 5 mm thick assemblies. The geometry was chosen to favor diffusion in the *x* direction (Figure 4). The length of this direction is shorter than the *z* direction and has been set at 10 mm to have a reasonable water diffusion time. The thickness of the substrates has been chosen so that their masses are not too large in relation to the adhesive in order to be able to measure a sufficiently large change in mass during ageing. The substrates were cut from stainless steel sheets with the following dimensions: 10 x 70 x 1 mm^3 and 10 x 80 x 1 mm^3 (Figure 4).

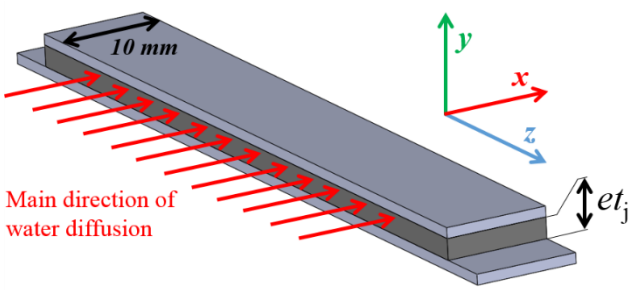

Figure 4. Sample geometry of bonded assembly and main direction of water diffusion

These substrates were then sandblasted and degreased with Methyl ethyl ketone (MEK). All assemblies were manufactured using the same substrates, surface preparation, adhesive and manufacturing cycle.

In order to compare the diffusion kinetics in bonded assembly and in bulk adhesive (and to validate the hypothesis ...), samples of bulk adhesive discs were also manufactured with the following dimensions: 70 mm diameter and 2 mm thick. With these dimensions, the interpretation of the results is facilitated. Indeed, diffusion can be considered mainly unidirectional in the thickness direction (thickness <<< diameter).

3.2 Gravimetric tests

To ensure good reproducibility of the tests, five samples of each thickness for the bonded joints and six samples for the bulk adhesive were carried out. After the manufacturing, they were conditioned for two weeks at 40 °C with a humidity level close to 16 % to ensure the lowest and most uniform water content possible.

For the ageing, samples are immerged in distilled water at 40 °C. The samples were taken periodically, dried on the surface and weighed with a precision balance (≈10^{-5} g), before being immerged back into water. Using the equation (4), it is possible to calculate the macroscopic water content *C(t)* of adhesive.

$$C(t) = \frac{m(t) - m_0}{m_0}.100 \qquad (4)$$

where *m(t)* and m_o respectively represent the mass of the adhesive during immersion and the initial mass.

The gravimetric tests make it possible to determine water diffusion kinetic. They exist several kinetics of water diffusion within polymeric and composite materials, these kinetics are listed in Weitsman's work [20].

4. Results and discussions

4.1 Water diffusion kinetics in a bulk adhesive

To determine the water diffusion kinetics in the bulk adhesive, six discs were immersed in distilled water at 40 °C and the evolution of the mass using a precision balance (≈10^{-5} g) has been measured periodically. Using the equation (4), the evolution of the macroscopic water content *C(t)* could be determined (Figure 5).

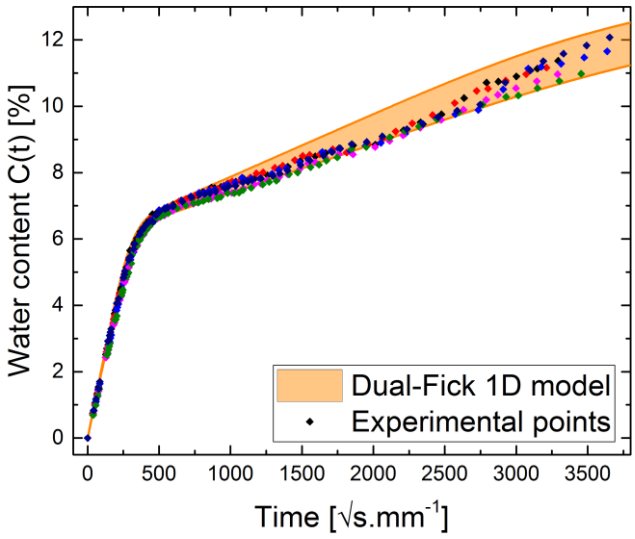

Figure 5. Sorption kinetics of the bulk adhesive during immersion water at 40 °C

The results in Figure 5 show a first linear phase. Then, the water content continues to increase more slowly. After 700 days of immersion, the curve still does not stabilize showing that saturation has not yet been reached. The change in slope to about 7 % water content, shows that the sorption kinetics is moving away from the Fick model, the most commonly used model. In this study we decided to use the Dual-Fick model [21]. The Dual-Fick model is based on the assumption that two diffusion processes occur simultaneously, with different speeds and maximum absorption capacities. In the unidirectional case, considering two Fick processes in parallel with coefficients D_1 and D_2 and water contents $c_1(x,t)$ and $c_2(x,t)$ the Dual-Fick model corresponds to the equation (5).

$$\frac{\partial c_1(x,t)}{\partial t} + \frac{\partial c_2(x,t)}{\partial t} = D_1.\frac{\partial^2 c_1(x,t)}{\partial x^2} + D_2.\frac{\partial^2 c_2(x,t)}{\partial x^2} \qquad (5)$$

In the unidirectional case, considering an initially dry material, the local resolution of the equation (5) is given by the equation (6) and allows to calculate the local water content $c(x,t)$:

$$c(x,t) = \sum_{i=1}^{2}\left[C_{\mathrm{si}}\left(1 - \frac{4}{\pi}\sum_{n=0}^{\infty}\frac{(-1)^n}{2n+1}exp\left[-(2n+1)^2\pi^2.\frac{D_{\mathrm{i}}.t}{e^2}\right]cos\left[(2n+1)\pi\frac{x}{e}\right]\right)\right] \qquad (6)$$

where D_1; D_2 represent the water diffusion and C_{s1}; C_{s2} represent the maximum of water absorption.

By integrating the equation (6) on the volume, the global water content $C(t)$ can be calculated (7).

$$C(t) = \sum_{i=1}^{2}\left[C_{si}\left(1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}exp\left[-(2n+1)^2\pi^2.\frac{D_i.t}{e^2}\right]\right)\right] \qquad (7)$$

It is this quantity that is measured experimentally during gravimetric tests, to identify the parameters of the Dual-Fick diffusion model, this analytical equation (7) was used. Identification was performed on each specimen by minimizing the least square deviation. By averaging the results and calculating a standard deviation, it is possible to plot a response spectrum (Figure 5). The identified parameters are listed in Table 1.

D_1 (mm².s^{-1})	(1,74 ± 0,04).10^{-6}
C_{s1} (%)	5,95 ± 0,03
D_2 (mm².s^{-1})	(9,01 ± 1,10).10^{-9}
C_{s2} (%)	7,23 ± 0,45

Table 1. Identified parameters of the Dual-Fick diffusion model

4.2 Water diffusion kinetics in a bonded joint

Gravimetric tests provide the following results. The water content $C(t)$ corresponds to the variation in mass with respect to the initial mass of the adhesive of the bonded assembly. An average and a standard deviation on the five specimens were calculated for each immersion time (Figure 6). In order to compare the kinetics of the assemblies with that of the bulk adhesive, the black curve was computed from the model parameters identified on the bulk to estimate the water diffusion through a sample of the same thickness as the bonded assemblies considering unidirectional diffusion (x direction).

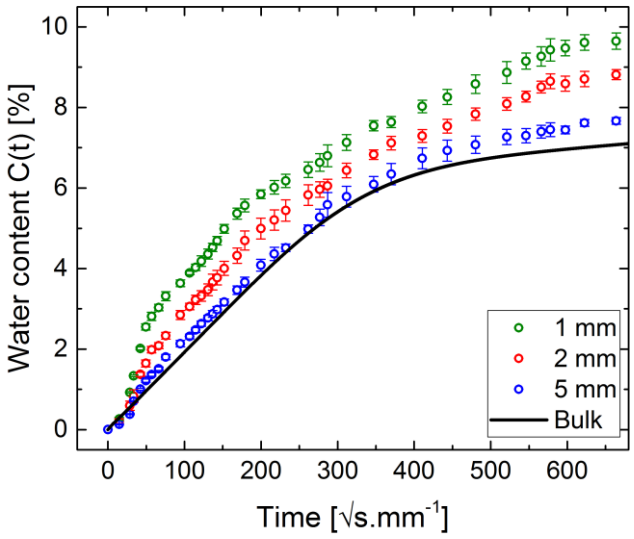

Figure 6. Evolution of the macroscopic water content as a function of immersion time for different bonded joint thickness

The results in Figure 6 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.

To macroscopically simulate this water content behavior of the assembly, it is necessary to know the diffusive characteristics of the interphase. For this purpose, the dual layer model that has been set up previously will be used.

4.3 Analytical solutions of the dual layer model

The quantity W be representing the square deviation in the least squares sense that must be minimized in this optimization problem for an instant t.

$$W = \sum_j \left[C_{\mathrm{j,exp}} - C_{\mathrm{j}}\right]^2 = \sum_j \left[C_{\mathrm{j,exp}} - \left(Cb_{\mathrm{j}} + \frac{2ei}{et_{\mathrm{j}}}(Ci - Cb_{\mathrm{j}})\right)\right]^2 \quad (8)$$

In order to optimize this problem, it is necessary to reduce the quantity *W* by minimizing this quantity in relation to the variables *Ci* and *Cb* that must be determined.

$$\frac{\partial W}{\partial Cb} = 0 \; ; \; \frac{\partial W}{\partial Ci} = 0 \quad (9)$$

By combining equations (8) and (9), it is possible to express an analytical solution of this minimization problem in the least squares sense, by determining the water content in original adhesive layer *Cb(t)* and in the interphase layer *Ci(t)*.

$$Cb(t) = \frac{\sum_{\mathrm{j}} \frac{1}{et_{\mathrm{j}}} \sum_{\mathrm{j}} \frac{C_{\mathrm{j}}(t)}{et_{\mathrm{j}}} - \sum_{\mathrm{j}} \frac{1}{et_{\mathrm{j}}^2} \sum_{\mathrm{j}} C_{\mathrm{j}}(t)}{\left(\sum_{\mathrm{j}} \frac{1}{et_{\mathrm{j}}}\right)^2 - \sum_{\mathrm{j}} \frac{1}{et_{\mathrm{j}}^2} \sum_{\mathrm{j}} 1} \quad (10)$$

$$Ci(t) = \frac{\sum_{\mathrm{j}} C_{\mathrm{j}}(t) - \sum_{\mathrm{j}} Cb(t)}{2ei \sum_{\mathrm{j}} \frac{1}{et_{\mathrm{j}}}} + Cb(t) \quad (11)$$

It is interesting to note that the analytical expression *Cb(t)* does not depend on any characteristic of the interphase but only on the total water content of the assembly $C_{\mathrm{j}}(t)$ and its thickness et_{j}. On the contrary, the analytical expression of *Ci(t)* depends on the thickness of the interphase *ei*. In conclusion, these analytical equations make it possible to calculate the water content of each layer in a direct way only with the results of the gravimetric tests.

4.4 Water diffusion within the interphase and original adhesive layers of the dual layer model

In this part the objective is to determine the water contents *Cb(t)* and *Ci(t)* of each layer using the analytical equations expressed above.

For the water content of the original adhesive layer noted as *Cb(t)*, it can be directly determined using the equation (10) and the experimental results (Figure 6).

Concerning the water content within the interphase *Ci(t)*, its thickness *ei* must be fixed. For this purpose, we used a previous study [12]. In this study, refractive index measurements in a bonded assembly were performed using a fiber optic sensor based on Fresnel reflection. The sensors were positioned at different distances to the substrate and the refractive index can be plotted as a function of this distance. The refractive index stabilizes at a distance of 250 ± 50 µm from the substrate.

To calculate the water content in the interphase part *Ci(t)*, the thickness of the interphase *ei* was initially set at 250 µm. The Figure 7 shows the evolution of the *Cb(t)* and *Ci(t)* concentrations calculated using the analytical solutions previously implemented (equations (10) and (11)).

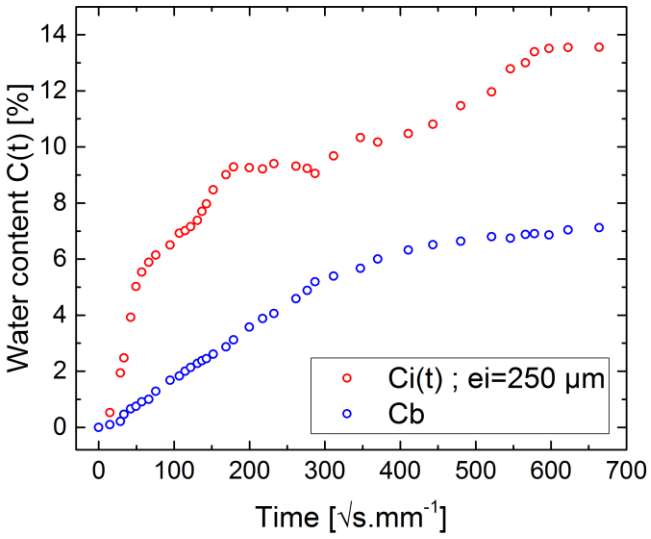

Figure 7. Evolution of the water content *Cb(t)* and *Ci(t)* as a function of immersion time, calculated using the dual layer model

The results show a significant difference between the *Cb(t)* and *Ci(t)* water contents. Indeed, water diffusion is faster but also more important in the interphases than at the core of the assembly. There is then a significant water content gradient between the two layers of this model. The difference in speed and amount of water absorbed between the interphase and the core comes from two contributions and has been explained above.

To represent these results, the analytical solution of the Dual-Fick model is used (7), this equation giving the expression of the global water content as a function of time. Identification was performed on each specimen by minimizing the least square deviation (Figure 8).

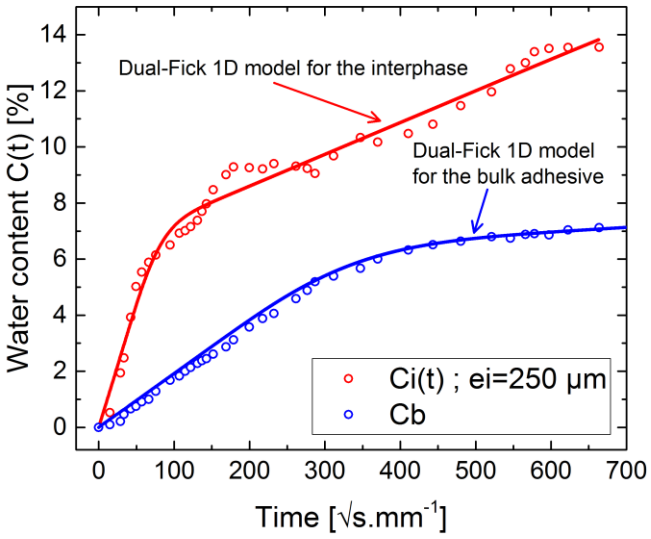

Figure 8. Identification with Dual-Fick model on the water content *Cb(t)* and *Ci(t)*

The identified parameters of Dual-Fick model are listed in Table 2.

Parameters	**Bulk adhesive**	***Cb(t)***	***Ci(t)***
D_1 (mm².s^{-1})	(1,74 ± 0,04).10^{-6}	1,74.10^{-6}	2,89.10^{-5}
C_{s1} (%)	5,95 ± 0,03	5,95	6,34
D_2 (mm².s^{-1})	(9,01 ± 1,10).10^{-9}	9,01.10^{-9}	1,43.10^{-7}
C_{s2} (%)	7,23 ± 0,45	7,23	13,27

Table 2. Parameters identified by the Dual-Fick model for water diffusion in both layers of the model. Black: diffusive parameters of the bulk adhesive; Blue: diffusive parameters of the original adhesive layer of the model; Red: diffusive parameters of the interphase layer of the model

The identified parameters (Table 2) represent the diffusive parameters of each layer of the model. First of all, it is important to note that these parameters for the original adhesive layer *Cb(t)* are identical to those of the bulk adhesive. At the core of the assembly, the water diffusion is therefore equivalent to that observed on the bulk adhesive.

The results show a significant difference between the parameters of each layer of the model. The diffusion coefficients are higher in the interphase, so the diffusion is faster. In addition, saturation water levels are also higher. To verify the good performance of this model, it is possible, using these parameters, to go back to the macroscopic water content of the assembly in order to compare the results with the gravimetric tests

4.5 Macroscopic water content of the bonded joint

Using the dual layer model with the parameters of each layer identified above, the objective is to go back to the macroscopic water content to verify if this model can model the gravimetric results (Figure 6). Using the parameters in Table 2 and the analytical solution of the Dual-Fick model (7), it is possible to determine the *Cb(t)* and *Ci(t)* moisture contents of each layer. Considering a 250 µm thickness interphase, only the proportion of interphase will change between the different thicknesses of the bonded joint. For a 1 mm, the interphase proportion is 50%, for 2 mm 25% and for 5 mm 10%. The macroscopic results obtained are shown in Figure 9 and compared with the gravimetric tests.

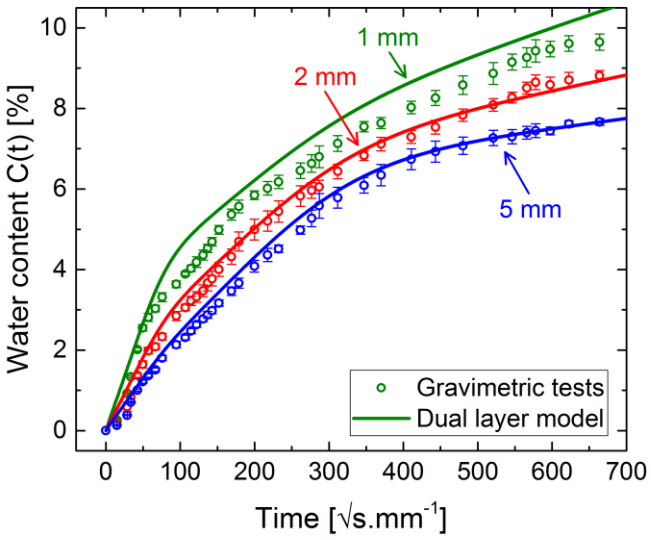

Figure 9. Evolution of water content in bonded assemblies, comparison between gravimetric tests and the dual layer model

In conclusion, this model makes it possible to represent, in a relatively reliable way, the macroscopic results obtained during gravimetric tests. However, there is an average difference of 11 % between the experimental data and the modelling for 1 mm assemblies.

In conclusion, this model mainly makes it possible to estimate and give an order of idea on the diffusive properties of interphases. On the other hand, its weak point comes from the need to

set an interphase thickness and therefore to make a strong hypothesis. To verify the model's dependence on this value, a sensitivity study was performed.

4.6 Sensitivity study of the model with the thickness of the interphase

As shown above, the interphase thickness can be between 200 and 300 µm. Previously the calculation was made for an interphase thickness of 250 µm. Thereafter, the same procedure is applied for a thickness of 200 and 300 µm. First, when calculating the water contents *Cb(t)* and *Ci(t)*, the results in Figure 8 change and are shown in Figure 10.

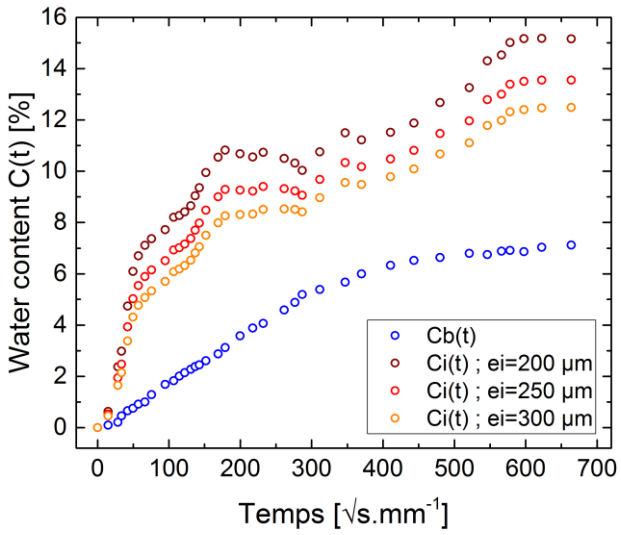

Figure 10. Evolution of the water content *Cb(t)* and *Ci(t)* as a function of immersion time, calculation carried out using the dual layer model considering three cases for the thickness of the interphase 200, 250 and 300 µm.

There is therefore a significant dependence of the water content *Ci(t)* on the thickness of the interphase. The lower is the thickness, the higher the water content is. However, we showed above on the analytical solution (10), the water content *Cb(t)* does not depend on this thickness.

As before, using the analytical solution of the Dual-Fick model (7), it is possible to identify the diffusive parameters of the two layers. In the case of the interphase, these parameters depend on the thickness of the selected interphase.

Parameters	Bulk adhesive	*Cb(t)*	*Ci(t)* *ei*=200 µm	*Ci(t)* *ei*=250 µm	*Ci(t)* *ei*=300 µm
D_1 (mm².s^{-1})	(1,74 ± 0,04).10^{-6}	1,74.10^{-6}	3,24.10^{-5}	2,89.10^{-5}	2,59.10^{-5}
C_{s1} (%)	5,95 ± 0,03	5,95	7,53	6,34	5,55
D_2 (mm².s^{-1})	(9,01 ± 1,10).10^{-9}	9,01.10^{-9}	2,11.10^{-7}	1,43.10^{-7}	1,20.10^{-7}
C_{s2} (%)	7,23 ± 0,45	7,23	15,03	13,27	10,73

Table 3. Parameters identified by the Dual-Fick model for water diffusion in both layers of the model. Black: diffusive parameters of the bulk adhesive; Blue: diffusive parameters of the original adhesive layer of the model; Red: diffusive parameters of the interphase of the model for the three cases of thickness considered (200, 250 and 300 µm).

For the interphase, the lower is the chosen thickness, the higher diffusion coefficients and the saturation water contents are. As before, the macroscopic water content of the assembly can be calculated by taking into account three different sets of diffusive parameters for the interphase.

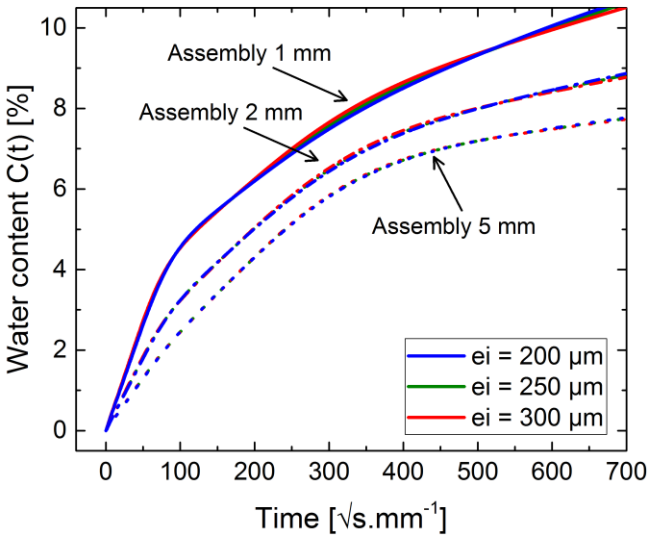

Figure 11. Comparison of the dual layer model on the calculation of the macroscopic water content for three interphase thicknesses: 200, 250 and 300 µm

Macroscopically, the Figure 11 shows a low dependence of the model on the different interphase thicknesses. The hypothesis realized on this value does not play an important role on the macroscopic water content of the assembly but on the diffusive properties of the interphase. Indeed, if we represent the local water content in the thickness of the assembly for different interphase thicknesses, the Figure 12 can be represented.

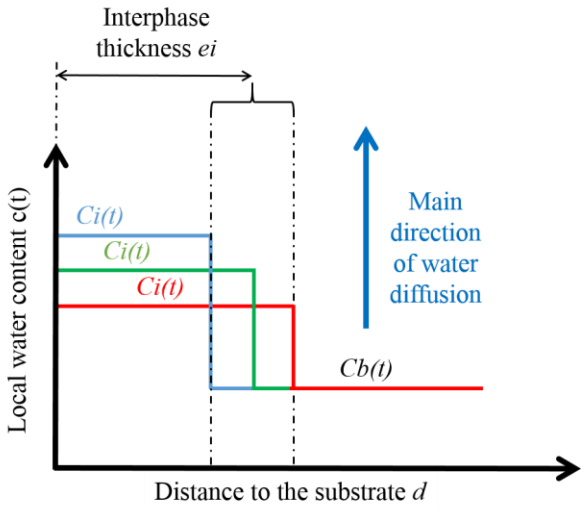

Figure 12. Representation of the water content within a bonded assembly as a function of distance from the substrate for the dual layer model for different interphase thicknesses

The local water content profile is therefore highly dependent on the thickness of the selected interphase. However, by integrating this local water content, it is possible to determine the macroscopic water content, which in the end does not depend on this thickness. In conclusion, the dual layer model allows to model the macroscopic water content of a bonded joint. However, since the assumptions made in this model are quite strong, there is no point in going back to the local water content field. This requires a more detailed characterization of the interphases.

5. Conclusion

First, gravimetric tests performed on several assembly thicknesses show a change in water diffusion kinetics in the bonded joint compared to the bulk adhesive. Indeed, the diffusion kinetics is faster and the water absorption is more important than on the bulk adhesive. This difference in kinetics comes from the presence of interphase which plays an important role in the water uptake of a bonded assembly. It is therefore essential to characterize the diffusive properties of the interphases.

For this purpose, the analytical model used is based on breaking down the adhesive joint into two layers: a layer at the core of the assembly that has the diffusive characteristics of the bulk adhesive and a layer that corresponds to the interphase. Based on the quantities of water present in these two layers, it is possible to go back to the diffusive parameters of the interphase by making a hypothesis about its thickness. In conclusion, this model makes it possible to model the macroscopic water uptake observed during gravimetric tests. However, it does not allow the determination of the local water content field.

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