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Corentin Humeau, Peter Davies, Frédéric Jacquemin. Moisture diffusion under hydrostatic pressure in composites. *Materials & Design*, 2016, 96, pp.90-98. 10.1016/j.matdes.2016.02.012 . hal-04200778

HAL Id: hal-04200778

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Moisture diffusion under hydrostatic pressure in composites

Corentin Humeau^{a,b,*}, Peter Davies^a, Frédéric Jacquemin^b

^a IFREMER Centre Bretagne, Marine Structures Laboratory, 29280 Plouzané, France

^b University of Nantes, Research Institute in Civil Engineering and Mechanics, 44600 Saint-Nazaire, France

Water diffusion under hydrostatic pressure is critical for many underwater applications. Nevertheless it has rarely been studied, and published data are contradictory. The aim of this study is to understand what governs pressure effects by studying different materials (unreinforced resin, and three glass-fibre reinforced epoxy composites). First, kinetics of water diffusion, for unreinforced resin and composite materials, are identified at different pressure levels (1, 50 and 500 bar). For the neat epoxy resin the water uptake remained unchanged when pressure was raised. The glass fibre reinforced epoxy composites produced by hand lay-up have a saturation level that increases significantly with increasing pressure, while the diffusion coefficient is unaffected. The in-fused composites show only a small effect of pressure slowing initial diffusion rate, while the prepreg composite show no effect. In a second part, the present study focuses on the identification of the diffusion law using a numerical method. In the final section X-ray micro-tomography is used and reveals a high level of porosity in the hand lay-up composite. Moreover, as glass fibres are hydrophobic and resin water uptake does not depend on hydrostatic pressure it is concluded that additional water diffuses into voids under pressure.

1. Background

The maximum service depth of composite use is constantly increasing in applications such as submarines, subsea oil industry structures or oceanographic profilers. Moisture diffusion in immersed composites is well known [1, 2] and its influence on mechanical properties has been studied [3–8]. However, when we consider the moisture uptake coupled with hydrostatic pressure a general trend cannot be established. While models [9, 10] tend to predict lower moisture uptake at higher pressure, experimental results can show increases [10], no effect [11], or reductions [9, 11, 12]. The aim of this work is to perform representative tests in order to understand this coupled phenomenon. Large differences in diffusion behaviour have been noted for different types of polymers. Pollard and al. in [13] established a linear relationship between pressure and moisture content in saturated glass fibre reinforced polyester.

Other studies have focused on less common matrix resins: Whitaker and al. studied in [14] the combined influence of pressure and temperature on the diffusion parameters in a polyester containing styrene monomer. In this case, pressure reduces the diffusion coefficient in the specimens only for temperatures over 25 °C, and has no influence on moisture saturation level.

Nevertheless, even for identical materials differences still exist, mainly induced by processing differences. For example, Avena and

Bunsell in [11] studied the effect of hydrostatic pressure on water diffusion in two types of glass fibre-reinforced composite based on the same epoxy resin reinforced either with un-sized fibres or with fibres treated with an organosilane size. Specimens were in the form of rectangular plates (150 × 25 mm), 0.73 mm thick and with a fibre volume fraction of 60%. Tests were performed in distilled water at 23 °C under hydrostatic pressures of 1, 50, 100 and 200 bar.

Under these conditions the two materials reacted in a different way to pressure: for un-sized fibres samples, the diffusion coefficient and saturation level decreased with pressure rise whereas, for treated fibres, both diffusion parameters remained unchanged with respect to pressure variations. This clearly showed that the fibre/matrix interface can play a role in moisture ingress under pressure.

Davies et al. in [10] tested a filament wound carbon fibre-reinforced epoxy under a hydrostatic pressure of 100 bar at 60 °C for 3.5 years. Specimens were square plates (50 × 50 mm) with a thickness of 3 mm. Their study showed a significant rise in saturation level with pressure rise for specimens either dry or previously saturated without pressure (Fig. 1).

These studies illustrate the difficulty in establishing a clear, unique influence of the hydrostatic pressure on the water diffusion even for one type of material. Considering this background, the following work considers three aspects. First, the experimental procedure is described: materials used, testing conditions, measurements, and first weight gain results are presented. Then the second part is devoted to the identification of the water diffusion laws and constants for each condition. Finally parameters which influence the water diffusion under pressure are discussed.

* Corresponding author at: IFREMER Centre Bretagne, Marine Structures Laboratory, 29280 Plouzané, France

E-mail addresses: corentin.humeau@ifremer.fr (C. Humeau), peter.davies@ifremer.fr (P. Davies), frederic.jacquemin@univ-nantes.fr (F. Jacquemin).

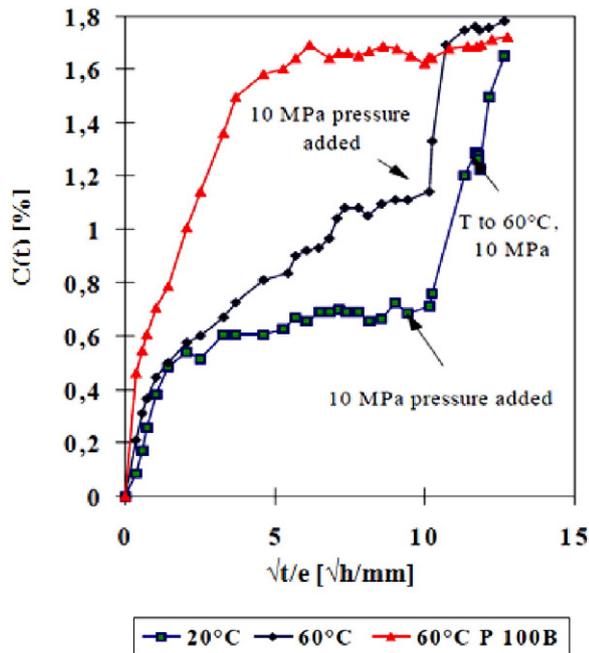


Fig. 1. Pressure influence on water diffusion in dried carbon/epoxy specimens (red) and in previously saturated specimens (blue) from [10].

Table 1
Materials tested.

Material	Thickness, mm	Vf	Tg	Porosity ratio
Epoxy resin	4.20 (\pm 0.20)	-	84 °C	\approx 0%
Hand lay-up composite	2.20 (\pm 0.10)	30%	80 °C	From 4% to 8%
Infused	2.25 (\pm 0.05)	58%	75 °C	1%
Prepreg	2.20 (\pm 0.02)	60%	110 °C	0.5%

2. Experimental

2.1. Experimental details

This study is mainly focussed on an epoxy resin and an E-glass reinforced composite with the same resin. Specimens were square plates (50 \times 50 mm) with the thicknesses shown in Table 1. For both types of specimen, the resin is the commercial epoxy SR1500 (mixture of DGEBA and DGEBF) with amine hardener SD2505 (from Sicomin, France) prepared by casting plates. Samples were post-cured for 6 h at 60 °C. Table 1 summarizes the initial material properties. The volume fraction of fibres (Vf) was calculated from TGA (thermogravimetric analysis) measurements in inert gas which provide the weight fraction

of resin. Glass transition temperatures (Tg) were established by a thermal technique (DSC, differential scanning calorimetry). Concerning porosity measurements, the method used is developed in section 4.

The first composite was reinforced with quasi-unidirectional glass fibres using hand lay-up, with a fibre content of 30% by volume. Two other composite materials with different epoxy resins were also tested for comparison, 2.25 mm thick infused and 2.20 mm thick pre-impregnated quasi-unidirectionally reinforced composites. The volume fractions for these were respectively 58% and 60% and the same fibre reinforcement was used for both. Fig. 2 shows micrographs of polished sections of the three composites.

Before immersion, all samples were dried at 60 °C for 15 days.

Pressure vessels (Fig. 3a and b) were manufactured to test specimens under pressures up to 1000 bar, and placed in an oven to regulate the temperature. These vessels were specially designed for rapid opening (threaded lid, see Fig. 3b), to limit measurement time. For this study, water diffusion was examined under atmospheric pressure (1 bar), low pressure (50 bar) and high pressures (250 and 500 bar) in order to highlight the effect of hydrostatic pressure. These tests on neat resin and hand lay-up composites were performed in tap water at 60 °C to increase kinetics and 5 specimens were tested in each condition. Samples were placed in racks to separate them (Fig. 3b). Reference specimens were placed in water in the same oven next to the pressure vessel. Tests on infused and prepreg materials came from a specific study in which specimens were immersed at 40 °C and 500 bars for 12 months. Again reference specimens were placed in the same oven without pressure. This second study was intended to extend the investigation to infused and prepreg glass-epoxy composites. Nevertheless these results cannot be directly compared to others performed at 60 °C.

In the case of composite materials the interfacial properties between fibres and resin can be critically affected by moisture uptake. To estimate the influence of pressure on the interfacial behaviour ILSS [15] and 4 point bending tests [16] were performed on both reference hand lay-up specimens and those subjected to pressure, after reaching saturation. Specimens tested had the following dimensions, for ILSS: 10 mm span, 15 mm \times 15mm square surface, and 2.5 mm thickness, and for 4 point bending: 60 mm span, 21 mm width and 2.5 mm thickness. Both series of tests were performed on an Instron test machine with a loading speed of 5 mm/min.

Microstructural details were first examined using optical microscopy (Leica DM ILM) on polished sections, with *ImageJ* software to quantify fibre and void contents.

X-ray micro-tomography studies were then performed to analyse the microstructure of four square plate specimens in each conditions. For these studies two types of system have been used:

- The GE Phoenix V-TOM-X240 which can analyse 50 \times 50mm specimens with a resolution of 28 mm³/voxel (for beam characteristics of 100 kV and 280 mA) – Fig. 12
- MicroXCT-400 from XRadia which can analyse samples of 25 \times 25mm with a resolution of 2 μ m (for beam characteristics of 60 kV and 133 μ A) – Fig. 15.

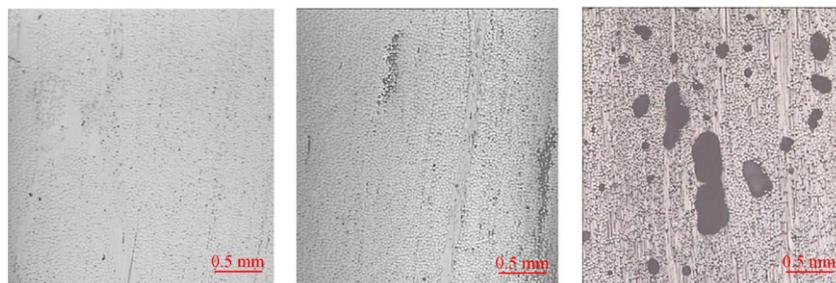


Fig. 2. Optical microscopy view of polished sections unidirectional prepreg (left), infused (centre) and hand lay-up (right) composites, sections perpendicular to fibre direction.

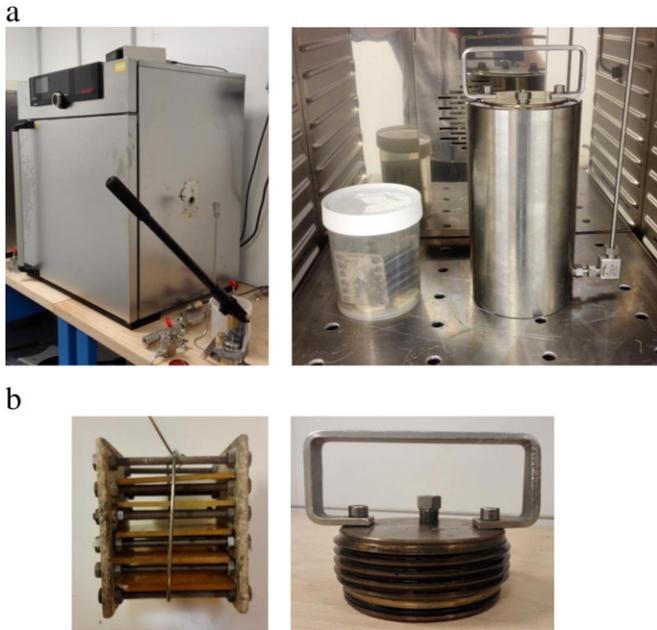


Fig. 3. a. Pressurisation system and ovens (left), pressure vessel (right). b. Specimens rack in the vessel (left) and specific lid for pressure uses (right).

2.2. Measurements and results

The water concentration by weight allows moisture diffusion in specimens to be characterised, it is defined as:

$$C(t) = \frac{\Delta M(t)}{M_0} \cdot 100 = \frac{M(t) - M_0}{M_0} \cdot 100 \quad (1)$$

With: $C(t)$ expressed in percent, $M(t)$ specimen weight at time t and M_0 initial specimen weight.

$M(t)$ is obtained by gravimetric measurements on a Sartorius balance (with precision of 10^{-4} g) made at periodic time intervals. In order to limit the influence of the handling time out of the pressure vessel on the water diffusion the maximum handling time was kept to $<5\%$ of the previous diffusion time.

Moisture content is shown as a function of time in Figs. 4 and 5. The moisture diffusion is plotted as percentage weight change versus square root of time. In a first approach, the diffusion coefficient was determined from the expression (Eq. (2)) valid for moisture content up to the half of

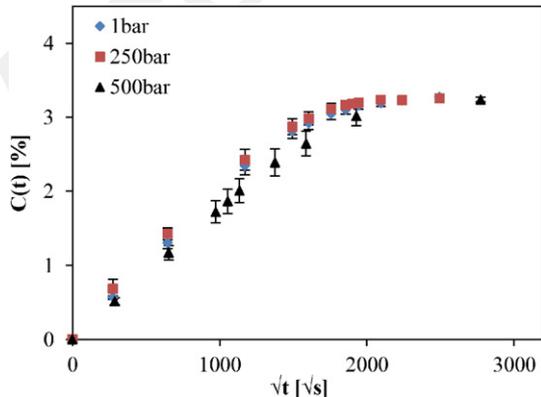


Fig. 4. Moisture uptake in resin at different pressures vs. square root of time.

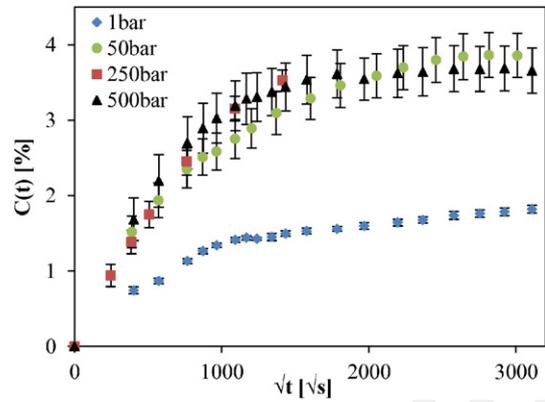


Fig. 5. Moisture uptake in glass fibre/epoxy composite under different pressures vs. square root of time. Error bars show standard deviation.

the water content in the saturated sample (Table 2).

$$D = \frac{\pi}{16 \cdot t} \cdot \left(\frac{M(t)}{M_\infty} \cdot d \right)^2 \quad (2)$$

With: d the thickness of the specimen.

In the case of neat resin specimens, water uptake at saturation is virtually unaffected by pressure rise (results in Fig. 4) and reaches 3% of the resin weight, a common value for epoxy resin. The diffusion coefficient, unaffected between 1 and 250 bar, diminishes slightly at 500 bar.

For hand lay-up glass fibre-reinforced epoxy, Fig. 5 represents the moisture content in the composite. For this composite ($V_f = 30\%$) with the matrix resin saturated with water the moisture content would correspond to 1.5% of the total composite weight. The influence of pressure on the moisture content is therefore significant (Fig. 5), water uptake is significantly higher at high pressure.

For atmospheric pressure the water uptake in the composite has a diffusion coefficient with a similar order of magnitude to that of the resin (Table 2), and moisture in saturated samples reaches 1.5% of composite weight, which corresponds to 3% of resin weight.

Fig. 6 shows the response of the infused and prepreg composites. For prepreg samples saturation level is not quite reached after 12 months at 40°C , and diffusion coefficients are established from saturation levels in similar specimens aged in water at atmospheric pressure.

For these higher fibre content materials 3% of weight gain in the resin corresponds to 0.73% in the composite, the water contents shown in Fig. 6 are slightly higher (around 1%) and saturation levels are not affected by pressure.

Diffusion coefficients in prepreg and infused composites are lower for high pressure: slightly lower for prepreg and significantly lower for infused samples (see Table 2).

The response of the materials to pressure is quite different. While moisture diffusion in neat epoxy and infused composite is unaffected by increasing pressure (Figs. 4 and 6), when this resin is reinforced with glass fibre by hand lay up the water content in saturated samples is significantly increased by pressure rise (Fig. 5). Diffusion coefficients

Table 2

Mean diffusion coefficient D (in 10^{-14} m^2/s) and 95% confidence interval estimated for each material and extreme pressure (1 and 500 bar).

Material type	Diffusion coefficient [10^{-14} m^2/s]	
	Pressure	
	1 bar	500 bar
Neat resin	123.2 ± 17.6	100.5 ± 3.9
Hand lay-up composite	97.4 ± 13.1	138.6 ± 19.6
Infused composite	18.5 ± 1.8	10.7 ± 2.0
Prepreg composite	4.0 ± 1.7	3.7 ± 1.1

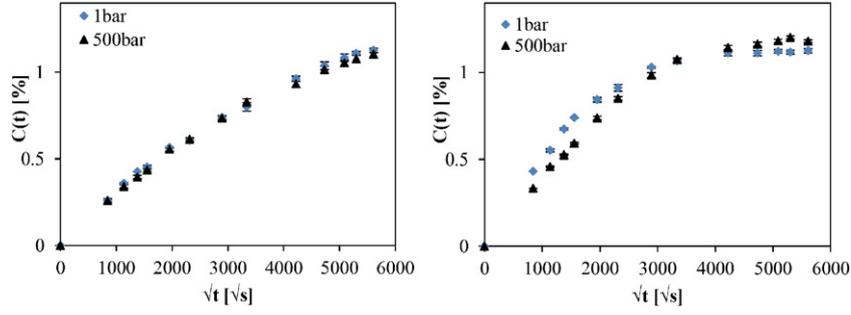


Fig. 6. Weight change kinetics of immersed prepreg (left), and Infused (right) composites with and without pressure at 40 °C.

are reduced by increasing pressure in all materials except in the hand layup composite where the diffusion coefficient under pressure exceeds the value in neat resin under atmospheric pressure.

The remainder of the study is focused on the pressure effect on hand lay-up composite, since this behaviour is not predicted by existing theories.

2.3. Influence of aging under pressure on mechanical behaviour

This significant difference in moisture diffusion could be induced by interfacial degradation between the resin and fibres. Results from ILSS and 4 point bending tests are quite sensitive to interfacial properties, so a series of tests was performed on saturated hand lay-up samples conditioned in the same 60 °C oven with and without 250 bar pressure, after saturation (50 days \approx 2000 \sqrt{s}). This is also of considerable practical importance for the design of deep sea structures, as it is the mechanical properties rather than weight gains which are needed for design. Fig. 7 shows the results.

Even though the immersion degrades the mechanical properties, results from these two tests after aging are not dependent on the amount of water uptake.

This suggests that aging at higher pressure does not affect the interface in these composite specimens. However, the hand lay-up composite results here and previous tests on filament wound samples [10] (Fig. 1) do indicate that moisture diffusion kinetics can be highly dependent on the type of material tested and the level of pressure applied to the specimen. The following section is focused on the identification of the diffusion laws in order to quantify the influence of pressure on each material.

3. Identification

Water uptake in resin and composites shows an initial linear increase with square root of immersion time, followed by a saturation plateau (Figs. 4 and 5). These characteristics can be related to Fickian diffusion behaviour to a first approximation.

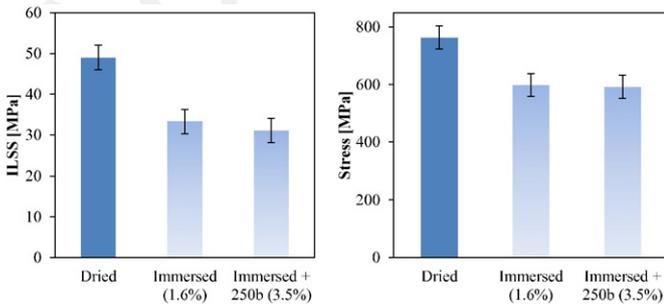


Fig. 7. Maximum stress obtained by ILSS (left) and 4 point bending (right) tests on composites dried and unaged, aged under atmospheric pressure ($C(\infty) = 1.6\%$), and aged under 250 bar of pressure ($C(\infty) = 3.5\%$).

3.1. Fickian diffusion

Fickian diffusion is usually defined by the relationship:

$$\vec{\varphi} = -D \vec{\text{grad}} c. \quad (3)$$

With $\vec{\varphi}$ the diffusive flux, c the moisture concentration and D the diffusion coefficient.

Fick's second law established the moisture distribution as a function of time (t) and position:

$$\frac{\partial c}{\partial t} = \text{div}(-D \vec{\text{grad}} c). \quad (4)$$

For the present study specimens are parallelepiped, Cartesian coordinates can be used to model this diffusion which will take place along the x , y and z axes, with x taken to be the fibre axis for the unidirectional composites. In this case Eq. (4) becomes:

$$\frac{\partial c}{\partial t} = D_x \frac{\partial^2 c}{\partial x^2} + D_y \frac{\partial^2 c}{\partial y^2} + D_z \frac{\partial^2 c}{\partial z^2}. \quad (5)$$

where D_x, D_y, D_z are respectively the diffusion coefficients along the axes x , y and z .

To obtain the expression of the total moisture content $C(t)$ (measured experimentally) Eq. (5) has to be integrated, and based on the work of Crank [17] we obtain:

$$\frac{C(t)}{C_\infty} = 1 - \left(\frac{8}{\pi^2}\right)^3 \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} \sum_{k=0}^{\infty} \frac{\exp\left(-\pi^2 t \left(D_x \left(\frac{2i+1}{L}\right)^2 + D_y \left(\frac{2j+1}{L}\right)^2 + D_z \left(\frac{2k+1}{L}\right)^2\right)\right)}{((2i+1)(2j+1)(2k+1))^2} \quad (6)$$

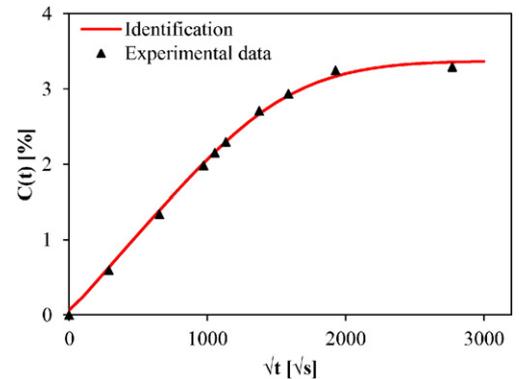


Fig. 8. Experimental and simulated moisture content in resin vs. root of time, one specimen 500 bars 60 °C.

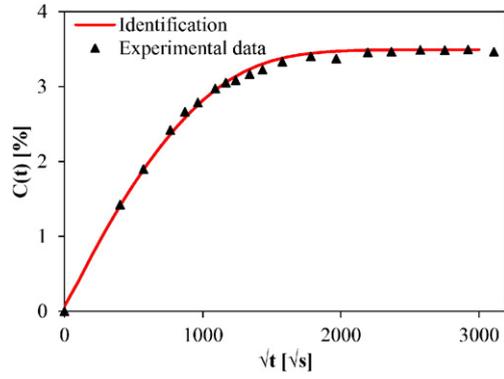


Fig. 9. Experimental and simulated moisture content in hand lay-up composite vs. root of time, one specimen 500 bars 60 °C.

In this expression, M_∞ represents the equilibrium moisture content in the saturated material, L , l and e are respectively the dimensions of the specimen along x , y and z axes.

The identification procedure is based on finding the 3D solution to Fick's equation which is as close as possible to the experimental values of weight gain during diffusion [18]. The method applied seeks the unknown variables of Eq. (6) by minimizing the standard deviation S (Eq. (7)) using a Gauss-Newton algorithm.

$$S = \sum_i [C(t_i) - C_i]^2 \quad (7)$$

With $M(t_i)$ the moisture content at time t_i from the simulation method and M_i the corresponding experimental value.

3.2. Identification method

In the general approach described above, diffusion coefficients were assumed to be different in the three directions. In the case of both neat resin and composite some simplifications can be made.

3.2.1. Neat resin

Epoxy specimens are considered as homogenous media, the diffusion coefficients are equal in all directions. If we consider $D_x = D_y =$

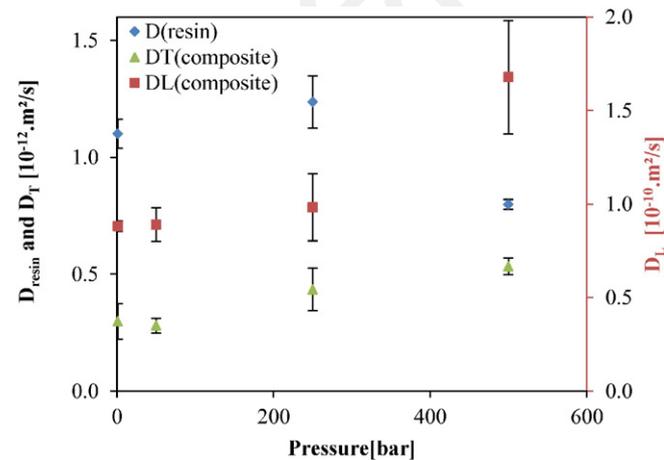


Fig. 10. Diffusion coefficient vs. pressure for glass/epoxy in longitudinal direction (right hand axis), transversal and in neat resin (right hand axis) for hand lay-up composite. NB Note large difference in scales for D_T and D_L .

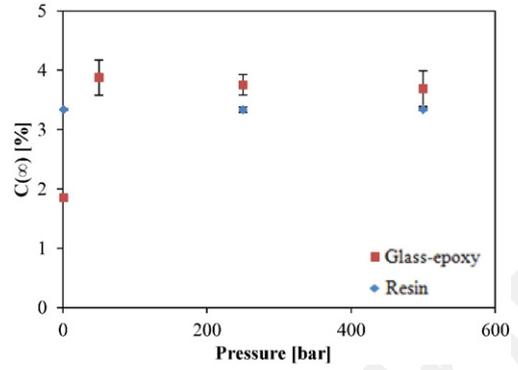


Fig. 11. Moisture content in specimens saturated specimens vs. pressure for resin and for the matrix resin of the glass-epoxy composite.

$D_z = D_{resin}$ Eq. (5) can be simplified:

$$\frac{\partial c}{\partial t} = D_{resin} \left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2} \right). \quad (8)$$

Then, the previous relationship is transposed to the identification method for the water uptake in each neat resin specimen under the different test pressures. The results obtained are quite conclusive, an example is presented in Fig. 8 for one neat resin specimen under 500 bar of pressure.

3.2.2. Glass fibre-reinforced epoxy

In unidirectional composites, the fibres introduce an equality between the diffusion coefficients along axes perpendicular to the reinforcements ($D_L = D_x$ and $D_T = D_y = D_z$), which leads to:

$$\frac{\partial c}{\partial t} = D_L \frac{\partial^2 c}{\partial x^2} + D_T \left(\frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2} \right). \quad (9)$$

This equation is established by considering x as the axis parallel to the fibre direction. This relationship was injected into the model identification for each composite sample and each environmental condition. The 3D Fickian simulation provides consistent values if we compare with experimental results (see Fig. 9).

3.3. Results

The identification process was performed for each specimen and at every pressure. In order to identify the influence of pressure on moisture uptake mechanisms, the diffusion coefficients and saturation levels are represented as functions of the pressure in Figs. 10 and 11. For each point the error bar represents the standard deviation between the 5 specimens tested under the same environmental condition.

For resin and composite the coefficient of diffusion is relatively stable from 1 bar to 250 bar. For a pressure of 500 bar the diffusion coefficients for both materials are significantly changed, with a decrease for the resin and a large increase for the composite (from $6.10^{-7} \text{ mm}^2/\text{s}$ to $1.10^{-6} \text{ mm}^2/\text{s}$).

For the neat resin, maximum water uptake does not depend on pressure level and remains at 3.5% of initial resin weight. This value does not deviate from one specimen to another (low maximum standard deviation = 0.03).

Moisture content in glass fibre-reinforced resin shows a significant rise between 1 and 50 bar, from 2% to 4% of the composite weight. For pressures over 50 bar water uptake in the composite does not depend on pressure.

After identification of the diffusion laws, the influence of pressure is clearly quite different between neat resin and composite. The next

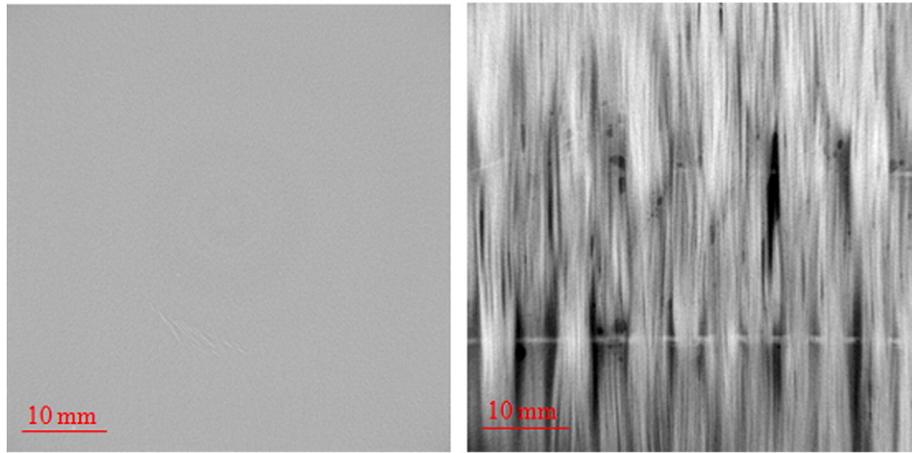


Fig. 12. Examples of tomographic images of a resin specimen (left) and a composite specimen (right) at the same scale (50 mm × 50 mm). Black regions indicate voids

Table 3
Porosity ratio for each specimen.

Pressure	Specimen	Porosity (%)
1 bar	1	6.0
	2	4.7
	3	5.3
	4	4.8
	5	5.0
50 bar	2	5
	3	4.7
	4	8.1
	5	6.4
	6	4.2
500 bar	1	4.5
	2	4.6
	3	4.9
	4	5.5
	5	4.4
	6	4.2

section is focused on the microstructural observations carried out in order to identify material parameters which could influence water diffusion in the resin, reinforced or not, at pressures up to 500 bar. The interpretation focuses on saturation levels, which have critical variations with pressure rise.

4. Discussion

4.1. Micro-structural analysis

To observe microstructures in resin and composite, each sample was analysed by X-ray micro-tomography. The observation of neat resin

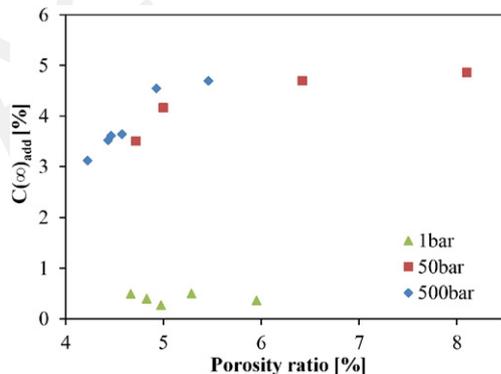


Fig. 13. $C^{(\infty)}_{add}$ after saturation in the composite vs. porosity ratio.

does not show any significant defects, the resin is transparent. However, in the case of glass fibre-reinforced epoxy the tomographic study showed a non-negligible porosity content (see Fig. 12 and Table 3). Voids are located in the region of the 90° weft fibres which maintain the 0° fibres. Fig. 12 shows micro-tomography images, values in Table 3 were obtained by image analysis of optical micrographs of polished samples taken from each specimen (based on 10 different measurements for each).

Since glass fibres are considered to be hydrophobic, water diffusion in the composite only takes place in the resin. This results in lower moisture content in composites than in neat resin. Experimental values confirm this phenomenon at 1 bar, but for higher pressures the composite takes up more water than the neat resin, which means that diffusion does not exclusively take place in the resin.

The additional diffusion which makes the composite more hydrophilic is related to a parameter absent in the neat resin. If the resin cure state is considered to be similar in both, and DSC measurements suggest this is the case, then there are only two main differences between the composite and resin materials studied here: the reinforcement and the porosity level. Reinforcements are hydrophobic and preliminary mechanical tests show interfacial properties are equally affected by water diffusion with and without pressure. We can therefore make the hypothesis that additional water uptake in the composite is located in voids.

To verify this assumption, the weight of water uptake in the composite $\Delta M_{glass-epoxy}$ will be separated into the water weight in the resin ΔM_{resin} and the additional water weight ΔM_{add} :

$$\Delta M_{glass-epoxy} = \Delta M_{add} + \Delta M_{resin} \quad (9)$$

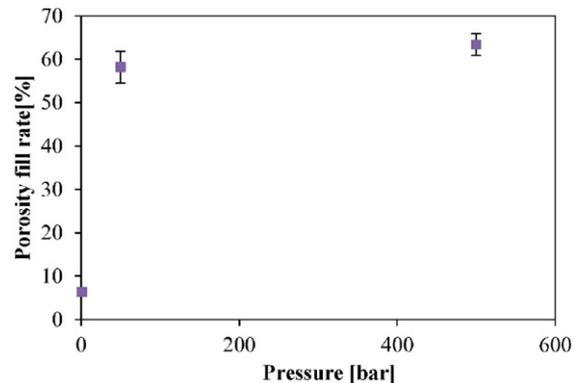


Fig. 14. Pore fill ratio after saturation at different pressures.

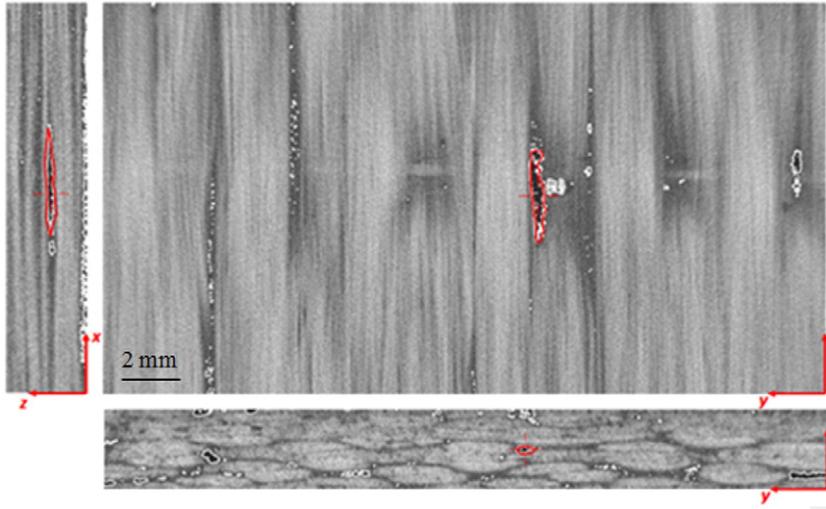


Fig. 15. Morphology of one porosity viewed in three directions - in red - (pictures from tomographic analysis).

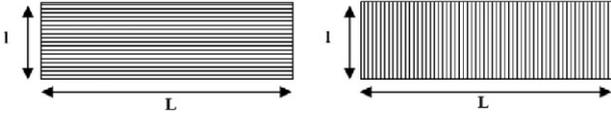


Fig. 16. Specimens used to examine longitudinal (left) and transverse (right) diffusion. With the following dimension: $L = 50$ mm, $l = 15$ mm, $d = 2.2$ mm.

with:

$$\Delta M_{resin} = \frac{\Delta M_{resin}}{M_{0-resin}} \cdot M_{0-resin} = C(t)_{resin} \cdot M_{0-resin} \quad (10)$$

$$\Delta M_{glass-epoxy} = C(t)_{glass-epoxy} \cdot M_{0-glass-epoxy} \quad (11)$$

The additional water uptake can be normalized with respect to the initial resin weight:

$$C(t)_{add} = \frac{\Delta M_{add}}{M_{0-resin}}(t) = C(t)_{glass-epoxy} \cdot X_{m_{resin}} - C(t)_{resin} \quad (12)$$

where $M_{0-resin}$ is the initial weight of resin in the composite and $X_{m_{resin}}$ is the weight ratio of resin in the composite.

Fig. 13 represents this new parameter ($C(t = \infty)_{add}$) as a function of the porosity ratio measured on each specimen.

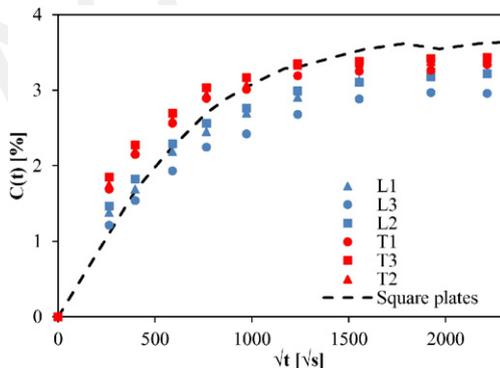


Fig. 17. Moisture diffusion in rectangular and square plates.

The additional water uptake in the composite ($C(\infty)_{add}$) shows a significant dependence on the porosity level established in Table 2 (Fig. 13). At atmospheric pressure, the presence of similar void levels does not influence water diffusion. As soon as pressure rises, water uptake increases in proportion to the porosity ratio.

The X-ray tomography analysis also highlights large variations of porosity ratio between specimens. To investigate the evolution of moisture diffusion into voids with pressure the pore fill ratio is used (a quantity independent of porosity ratio):

$$\text{Pore fill ratio (\%)} = \frac{\Delta V_{water-voids}}{V_{0-voids}} \quad (13)$$

$$\frac{\Delta V_{water-voids}}{V_{0-voids}} = \frac{\Delta M_{voids} \cdot \rho_{water}}{V_{0-voids}}$$

With $\Delta V_{water-voids}$ the volume variation of water inside voids, $V_{0-voids}$ the initial volume of porosities, and ΔM_{voids} the variation of water weight inside voids (Fig. 14).

The rise in pressure between 1 and 50 bar has the same effect on this parameter as on weight of water in porosities (Fig. 13), nevertheless when pressure rises from 50 to 500 bar, pore fill ratio is still increasing slightly. This further increase was not identified on other parameters (water weight or concentration), and suggests that increasing pressure from 50 to 500 bar results in more water being pushed into the pores.

4.2. Anisotropic analysis

Up to now we have considered porosity as a global measurement of free space, but the tomographic study highlighted a significant orientation of porosities along the fibre direction. Higher resolution tomography analyses confirmed this, (see Fig. 15), moreover Fig. 10 shows a diffusion coefficient along fibres (from a first approximation) 100 times higher than for resin or transverse diffusion.

Based on these observations a further study on rectangular plates has been conducted at 500 bars and 60 °C: diffusion has been studied in two types of hand lay-up composite specimens (see Fig. 16) to highlight the differences between transverse and the longitudinal diffusion.

Transverse specimens will be noted T_i and longitudinal ones L_i (with i the number of the specimen). Longitudinal specimens will have a diffusion coefficient highly dependent on the transverse diffusion coefficient, while the longitudinal coefficient will dominate diffusion in the transverse plates. Three samples of each specimen type were immersed at 500 bars, four 50×50 mm² square specimens were immersed with them as a reference.

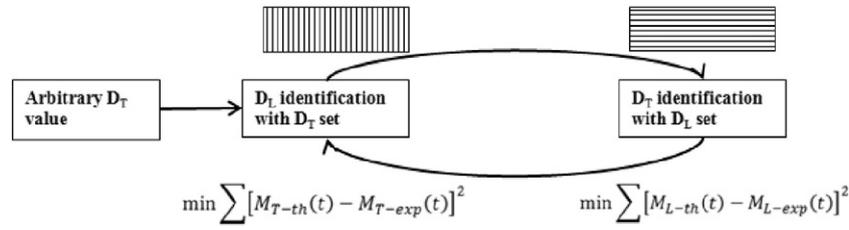


Fig. 18. Identification method of D_T and D_L from diffusion in rectangular plates.

Fig. 17 shows results obtained from this study, and it is clear that the diffusion kinetics are different for L and T specimen types. The transverse specimens show much faster diffusion kinetics than the other specimens.

As shown in Fig. 15 porosities are oriented along fibres, which could induce capillary effects and increase the longitudinal diffusion kinetics.

In order to quantify the diffusion coefficient variations due to aligned porosity, identification has been performed for these specimens. This identification is based on an iterative method as shown in Fig. 18:

- Diffusion in longitudinal plates is used to identify D_T by setting a constant D_L
- Diffusion in transverse plates is used to identify D_L by setting a constant D_T

The diffusion curves obtained from identification are consistent with experimental values (Fig. 19). In order to verify the identification, the

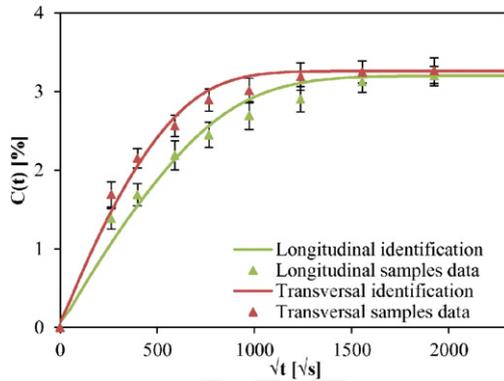


Fig. 19. Diffusion curves from identification compared to experimental values

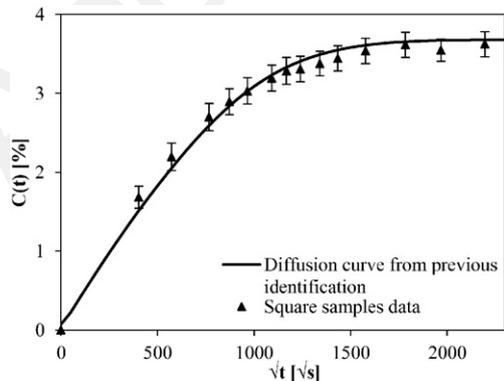


Fig. 20. Comparison between experimental moisture diffusion in square plates and diffusion curve established using D_T and D_L identified on rectangular plates

identified diffusion coefficients, given in Table 2, were entered into the moisture content equation of square plates. The predicted plot from this equation shows good agreement with experimental values of moisture content in the square specimens (Fig. 20).

In order to quantify the impact of porosities on diffusion kinetics, the identified coefficients from the rectangular specimens are compared in Table 4 to theoretical values. There are various micro-mechanics models to predict diffusion coefficients [20]. Here an expression based on the work of Shirrell and Halpin [19] was applied, $D_L = D_{resin}$ and $D_T = D_{resin} / (1 + v_f)$.

Table 4 shows that the transverse coefficient based on resin weight gain and fibre content is in good accordance with theory, whereas longitudinal diffusion is much higher than would be expected in a composite without porosity ($D_{L(identification)} > 40 \times D_{L(theory)}$).

5. Conclusion

An experimental study of weight gain by resin and three different types of glass fibre reinforced resin immersed in water at different pressures up to 500 bar showed significant differences in behaviour. The resin weight gain was not affected by pressure whereas the hand lay-up composite showed significantly higher weight gain under high pressure. The effect on infused composites was smaller and for prepreg no effect was noted. The hypothesis was made that, based on microscopy and micro-tomography analyses, porosity level influences water diffusion at high pressure. Correlation between measurements and observations verified this hypothesis. The higher weight gain under pressure did not affect mechanical properties in flexure. Finally, the morphological study of porosities led to the conclusion that their preferential orientation along the fibres influences the diffusion kinetics.

Further studies are underway which focus on the morphology of porosity before and after aging. Carbon/epoxy composites are also being studied.

Acknowledgements

The authors are grateful to Ifremer and the University of Nantes for their contributions to this project. The contribution of ONR via project N00014-14-1-0832 and project monitor Dr Y. Rajapakse, is also gratefully acknowledged. Thanks to Matt Dawson of Aviation Enterprises, UK, for the manufacture of the infused and prepreg composites. And a special thanks to Pierre-Yves Le Gac and Sylvain Fréour for helpful discussions.

Table 4

Diffusion coefficients (in m^2/s) obtained by identification compared with theoretical ones from [19].

	D_{RESIN}	D_L	D_T
Identification results	1.01×10^{-12}	4.91×10^{-11}	7.71×10^{-13}
Theoretical values		1.01×10^{-12}	7.77×10^{-13}

References

- [1] F.R. Jones, Durability of reinforced plastics in liquid environments, in: G. Pritchard (Ed.), *Reinforced Plastics Durability*, CRC Press 1999, pp. 70–110.
- [2] T.J. Searle, J. Summerscales, Review of the durability of marine laminates, in: G. Pritchard (Ed.), *Reinforced Plastics Durability*, CRC Press 1999, pp. 219–266.
- [3] J.D. Garcia-Espinel, D. Castro-Fresno, P. Parbole Gayo, F. Ballester-Muñoz, Effects of sea water environment on glass fiber reinforced plastic materials used for marine civil engineering constructions, *Mater. Des.* 66 (Part A) (2015) 46–50 Feb.
- [4] A. Hawa, M.S. Abdul Majid, M. Afendi, H.F.A. Marzuki, N.A.M. Amin, F. Mat, A.G. Gibson, Burst strength and impact behaviour of hydrothermally aged glass fibre/epoxy composite pipes, *Mater. Des.* 89 (Jan. 2016) 455–464.
- [5] Y. Zhong, S.C. Joshi, Impact behavior and damage characteristics of hygrothermally conditioned carbon epoxy composite laminates, *Mater. Des.* 65 (Jan. 2015) 254–264.
- [6] M. Assarar, D. Scida, A. EL Mahi, C. Poilâne, R. Ayad, Influence of water ageing on mechanical properties and damage events of two reinforced composite materials: flax-fibres and glass-fibres, *Mater. Des.* 32 (2) (Feb. 2011) 788–795.
- [7] Y.J. Weitsman, *Fluid Effects in Polymers and Polymeric Composites*, Springer Science & Business Media, 2011.
- [8] K. Berketis, D. Tzetzis, P.J. Hogg, The influence of long term water immersion ageing on impact damage behaviour and residual compression strength of glass fibre reinforced polymer (GFRP), *Mater. Des.* 29 (7) (2008) 1300–1310.
- [9] K. Derrien, P. Gilormini, The effect of moisture-induced swelling on the absorption capacity of transversely isotropic elastic polymer–matrix composites, *Int. J. Solids Struct.* 46 (6) (Mar. 2009) 1547–1553.
- [10] P. Davies, D. Choqueuse, F. Mazéas, Composites underwater, Presented at the Progress in Durability Analysis of Composites Systems, Balkema, Rotterdam 1997, pp. 19–24.
- [11] A. Avena, A.R. Bunsell, Effect of hydrostatic pressure on the water absorption of glass fibre-reinforced epoxy resin, *Composites* 19 (5) (Sep. 1988) 355–357.
- [12] B.E. Sar, S. Fréour, P. Davies, F. Jacquemin, Coupling moisture diffusion and internal mechanical states in polymers – a thermodynamical approach, *Eur. J. Mech. – A Solids* 36 (Nov. 2012) 38–43.
- [13] A. Pollard, R. Baggott, G.H. Wostenholm, B. Yates, A.P. George, Influence of hydrostatic pressure on the moisture absorption of glass fibre-reinforced polyester, *J. Mater. Sci.* 24 (5) (May 1989) 1665–1669.
- [14] G. Whitaker, M.I. Darby, G.H. Wostenholm, B. Yates, M.H. Collins, A.R. Lyle, B. Brown, Influence of temperature and hydrostatic pressure on moisture absorption in polymer resins, *J. Mater. Sci.* 26 (1) (Jan. 1991) 49–55.
- [15] D30 Committee, D2344: Test Method for Short-beam Strength of Polymer Matrix Composite Materials and Their Laminates, ASTM International, 2013.
- [16] D20 Committee, D790: Test Methods for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials, ASTM International, 2010.
- [17] J. Crank, et al., *The Mathematics of Diffusion*, Vol. 2 Clarendon Press, Oxford, 1975.
- [18] F. Pierron, Y. Poirette, A. Vautrin, A novel procedure for identification of 3D moisture diffusion parameters on thick composites: theory, validation and experimental results, *J. Compos. Mater.* 36 (19) (Oct. 2002) 2219–2243.
- [19] C.D. Shirrell, J. Halpin, Moisture absorption and desorption in epoxy composite laminates, *ASTM Spec. Tech. Publ.* 617 (1977) 514–528.
- [20] H.R. Dana, A. Perronnet, S. Fréour, P. Casari, F. Jacquemin, Identification of moisture diffusion parameters in organic matrix composites, *J. Compos. Mater.* 47 (9) (Apr. 2013) 1081–1092.