MOISTURE DIFFUSION UNDER PRESSURE IN COMPOSITES

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Keywords: Composite, Moisture diffusion, Hydrostatic pressure

ABSTRACT

The influence of hydrostatic pressure on composite behaviour is critical for many underwater applications. Under these extreme environmental conditions water diffusion 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, glass reinforced epoxy composites). First, water diffusion was studied at different pressure levels (1, 50 and 500 bar) in order to identify the diffusion models. For the neat epoxy resin the water uptake remained unchanged by pressure rise, whereas glass fibre reinforced epoxy had a maximum moisture content that increased while the diffusion coefficient was unaffected. In a second part, the present study focuses on the identification of the diffusion law using a numerical method. In the final section the analysis of microstructure revealed one influent parameter on the water diffusion in composites under pressure. Indeed, an X-ray micro-tomography study showed a high level of porosity in the glass fibre reinforced epoxy. Moreover, glass fibres are hydrophobic which results in water diffusion exclusively located in the resin and in voids in the composite. Whereas resin water uptake does not depend on hydrostatic pressure, the additional moisture content in voids showed a high dependence with pressure level and a link with porosity ratio in the composite.

1 CONTEXT

The maximum depth of composite use is constantly increasing in applications such as submarines, subsea oil industry structures or oceanographic profilers. Moisture diffusion for immerged composites is well known and its influence on mechanical properties has been studied. However, when we consider the moisture uptake coupled with hydrostatic pressure a general trend cannot be established. While models [1, 2] tend to predict lower moisture uptake at higher pressure, experimental results can show increases [3], no effect [4], or decreases [1, 2, 4]. The aim of this work is to perform representative tests in order to understand this coupled phenomenon.

Previous experimental research has shown different changes in water diffusion when pressure was increased.
For example, Avena and Bunsell worked on the effect of hydrostatic pressure on water diffusion in two types of glass fibre-reinforced epoxy resin [4] reinforced either with un-sized fibres (FV1) or with fibres treated with an organosilane size (FV2). Specimens were in the form of rectangular plates (150 x 25mm) 0.73mm 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 FV1 the diffusion coefficient and saturation level decreased with pressure rise whereas, for FV2, both diffusion parameters remained unchanged with respect to pressure variations (Figure 1).
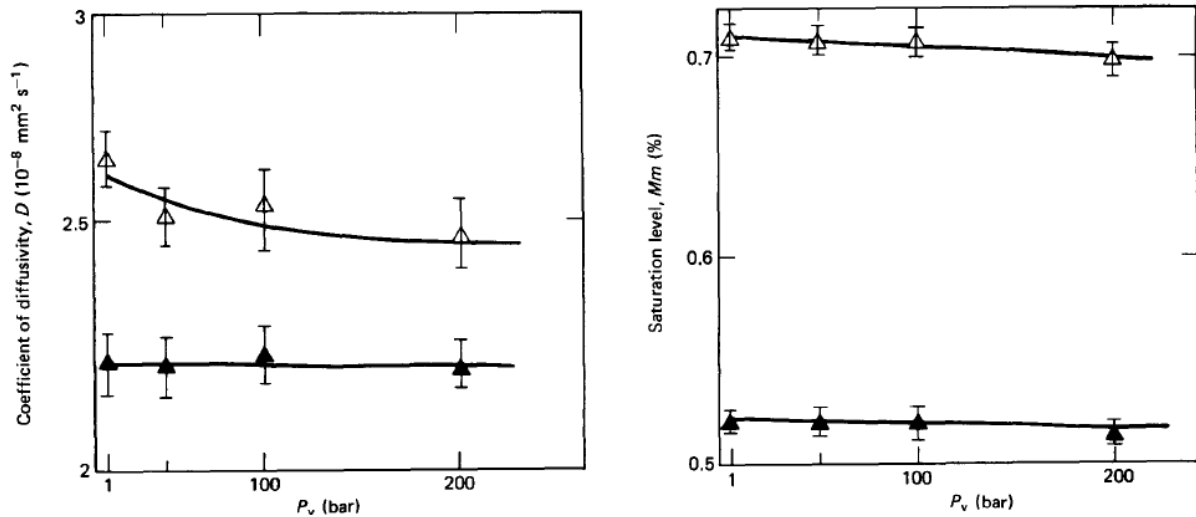

Figure 1: Pressure influence on diffusion coefficient (left) and saturation level (right) for FV1 (white) and FV2 (black) (from [4])

Davies and al. in [3] tested a filament wound glass fibre-reinforced epoxy under a hydrostatic pressure of 100 bar at 60°C. Specimens were square plates (50 x 50mm) with a thickness of 3mm.
Their study showed a significant rise in saturation level with pressure rise.

These two studies illustrate the difficulty in establishing a clear, unique influence of the hydrostatic pressure on the water diffusion.

Considering this background, the following work is structured around three aspects. First the experimental procedure is described: materials used, testing conditions, measurements, and first results. The second part is dedicated to the identification of the water diffusion laws and constants for each condition. Finally the emphasis will be on the parameters which influence the water diffusion under pressure.

2   EXPERIMENTAL STUDY

2.1   Experimental details

Specimens were square plates (50 x 50mm) with a thickness of 3mm, of neat epoxy and fibre-reinforced epoxy. For both types of specimen, the resin is the epoxy SR1500 with amine hardener SD2505 (from Sicomin) prepared by casting plates. The composite was reinforced with quasi-unidirectional glass fibres using hand lay-up, with a fibre content of 30% by volume.

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

Pressure vessels (Figure 2) 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, to limit measurement time. For this study, water diffusion was examined under atmospheric pressure (1 bar), low pressure (50 bar) and high pressure (250 and 500 bar) in order to highlight the effect of hydrostatic pressure. These tests were performed in tap water at 60°C to increase kinetics and 5 specimens were tested in each condition. Reference specimens were placed in water in the same oven next to the pressure vessel.

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 [5] and 4 point bending tests were performed [6] on both reference specimens and those subjected to pressure, after reaching saturation. Specimens tested had the following dimensions, for ILSS: 15mm x15mm square surface, and 2.5mm thickness, and for 4 point bending: 60mm span,

21mm width and 2.5mm thickness.

Figure 2: Pressure vessel in oven regulated at 60°C

2.2 Measurements and results

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

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

With: $C(t)$ expressed in percent, $M(t)$ specimen weight a time t and Mo initial specimen weight.
$M(t)$ is obtained by gravimetric measurements 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 less than 5% of the previous diffusion time.

Water concentration is shown as a function of time in figures 3 and 4. The moisture diffusion is plotted versus square root of time divided by thickness of the specimen, to account for specimen thickness variations.

In the case of neat resin specimens, water uptake is virtually unaffected by pressure rise (results in figure 3).
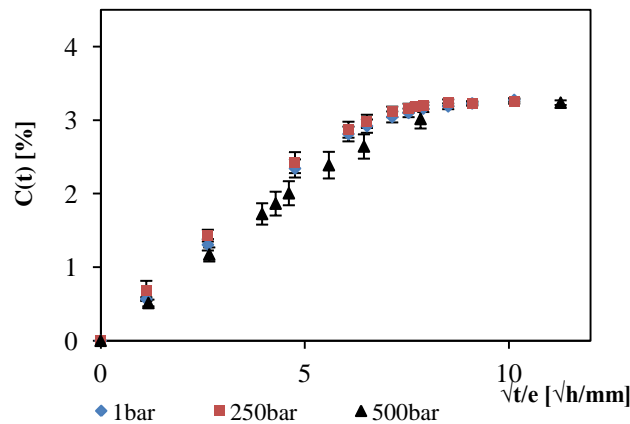

Figure 3 Moisture uptake in resin at different pressures vs. Square root of time divided by thickness

For glass fibre-reinforced epoxy, the influence of pressure on the moisture content is significant (figure 4), water uptake is significantly higher at high pressure.
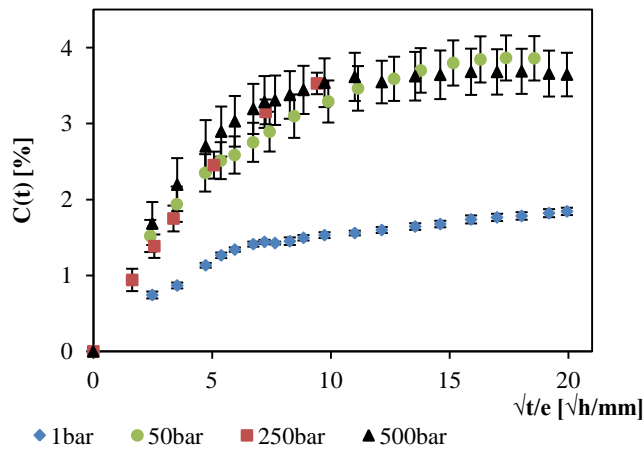
Figure 4: Moisture uptake in glass fibre/epoxy composite under different pressures vs. square root of time on thickness. Error bars show standard deviation.

The response of the two materials to pressure is quite different; while neat epoxy is unaffected, the water diffusion in this glass fibre-reinforced epoxy is significantly increased by pressure rise.

2.3 Influence of ageing 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 directly dependant on interfacial properties so a series of tests was performed on saturated samples conditioned in the same 60°C oven with and without 250 bar pressure. 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. Figure 5 shows the results.
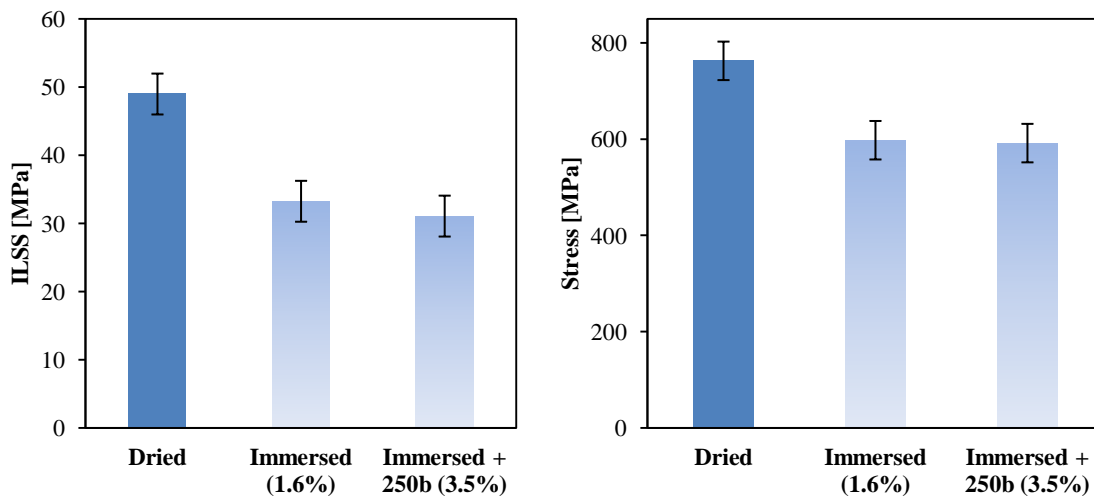

Figure 5: Maximum stress obtained by ILSS (left) and 4 point bending (right) tests on composites dried and unaged, aged under atmospheric pressure (C(∞)=1.6%), and aged under 250bar of pressure (C(∞)=3.5%)

Even though the immersion degrades the mechanical properties, results from these two tests are not dependant on pressure level.

This suggests that aging at higher pressure does not affect the interface in these composite specimens. However, moisture diffusion 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 to quantify the influence of pressure on each material.

3   IDENTIFICATION

Water uptake in resin and composite shows an initial linear evolution followed by a saturation plateau (figure 3 and 4). These characteristics can be related to Fickian diffusion behaviour to a first approximation.

3.1 Fickian diffusion

Fickian diffusion is usually defined by the relationship:

$$\vec{\varphi} = -D \overrightarrow{grad}\, C \tag{2}$$

With φ the diffusive flux, C the moisture content and D the diffusion coefficient.

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

$$\frac{\partial c}{\partial t} = div(-D \overrightarrow{grad}\, C) \tag{3}$$

For the present study specimens are parallelepiped (orthotropic plates), Cartesian coordinates are efficient to model this diffusion which will take place along the x, y and z axes. In this case the equation (3) becomes:

$$\frac{\partial C}{\partial t} = D_1 \frac{\partial^2 C}{\partial x^2} + D_2 \frac{\partial^2 C}{\partial y^2} + D_3 \frac{\partial^2 C}{\partial z^2} \tag{4}$$

Where D_1, D_2, D_3 are respectively the diffusion coefficients along the axes x, y and z.

To obtain the expression of the total moisture content *M(t)* (known experimentally) the equation (4) has to be integrated, and based on study **[7]** we have:

$$\frac{M(t)}{M_\infty} = 1 - \left(\frac{8}{\pi^2}\right)^3 \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} \sum_{k=0}^{\infty} \frac{exp\left(-\pi^2 t \left(D_1 \left(\frac{2i+1}{L}\right)^2 + D_2 \left(\frac{2j+1}{l}\right)^2 + D_3 \left(\frac{2k+1}{e}\right)^2\right)\right)}{\left((2i+1)(2j+1)(2k+1)\right)^2} \tag{5}$$

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.

The identification procedure is based on finding the 3D Fick's solution as close as possible to experimental values of weight gain during diffusion [8]. The method applied seeks unknown variables of the equation (5) by minimizing the standard deviation S (Equation (6)) using a Gauss-Newton algorithm.

$$S = \sum_i [M(t_i) - M_i]^2 \tag{6}$$

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 previous method, diffusion coefficients were assumed to be different in the three directions. In the case of both neat resin and composite simplifications can be made.

Neat resin:

Epoxy specimens are considered as homogenous media, the diffusion coefficients are equal in all directions. If we consider $D_1=D_2=D_3=D$ the equation (4) is modified:

$$\frac{\partial C}{\partial t} = D \left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2} \right) \tag{7}$$

Then, the previous relationship is transposed to the identification method for the water uptake in each neat resin specimen under the different tested pressures. Results obtained are quite conclusive, an example is presented figure 6 for one neat resin specimen (number1) under 500 bar of pressure.
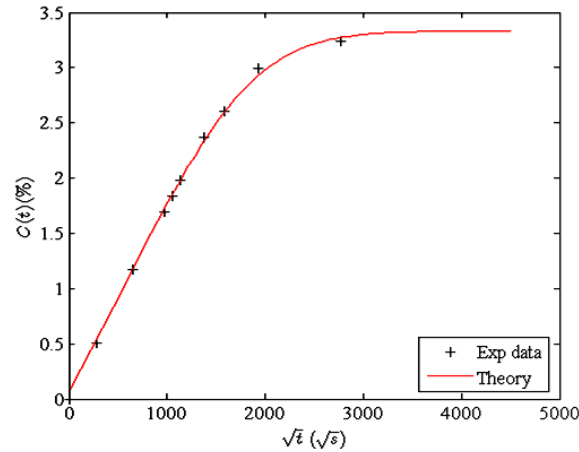

Figure 6: Experimental and simulated moisture content in resin vs. root of time

Glass fibre-reinforced epoxy:

In unidirectional composites the fibres induce an equality between the diffusion coefficients along axes perpendicular to reinforcements ($D_{//} = D_x$ and $D_\perp = D_y = D_z$), which induces :

$$\frac{\partial C}{\partial t} = D_{//} \frac{\partial^2 C}{\partial x^2} + D_\perp \left(\frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2} \right) \tag{8}$$

This equation is established by considering *x* as the axis parallel to the fibre direction. This relationship was injected into the model identification for every composite sample and each environmental condition. The 3D Fickian simulation provides consistent values if we refer to experimental results (see figure 7)
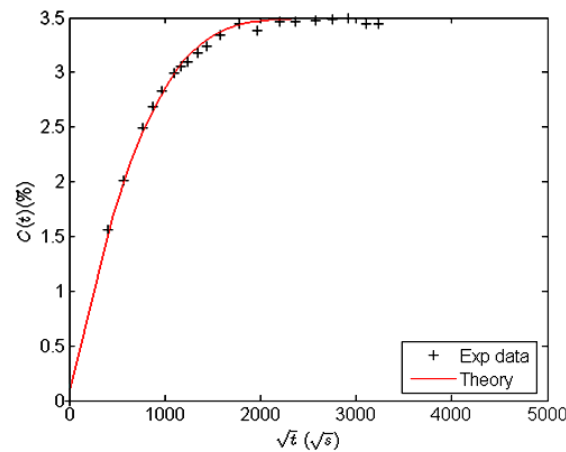

Figure 7: Experimental and simulated moisture content in composite vs. root of time

3.3 Results

The identification process was performed for each specimen and at every pressure. In order to identify the pressure influence on moisture uptake mechanisms, the diffusion coefficients and saturation levels are represented as functions of the pressure in Figures 8 and 9. For each point the error bar represents the standard deviation between the 5 specimens tested in the same environmental condition.
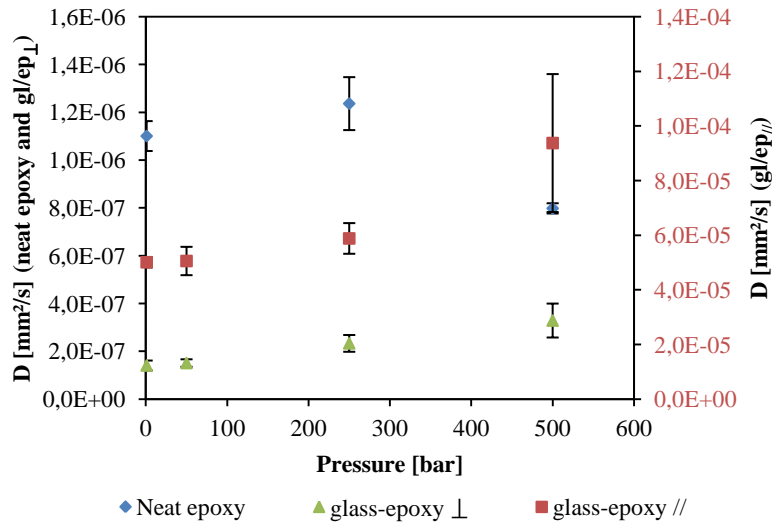
Figure 8: Diffusion coefficient vs. pressure for resin and glass/epoxy composite

For resin and composite the coefficient of diffusion is relatively stable from 1 bar to 250 bar. For 500 bar of pressure the diffusion coefficient for both materials is significantly changed, with a decrease for resin and a large increase for composite (from 6.10^{-7} mm²/s to 1.10^{-6} mm²/s).
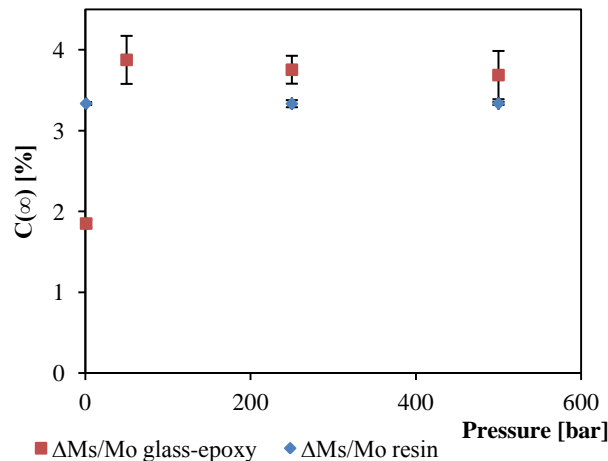
Figure 9: Moisture content in specimens saturated vs. pressure for resin and glass-epoxy composite

For the neat resin, maximum water uptake does not depend on pressure level and stays equal to 3.5% of 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 section is focused on the microstructure observations 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   INTERPRETATION

To observe microstructures in resin and composite, each sample was analysed by X-ray micro-tomography. The observation of neat resin does not show any significant defects. However, in the case of glass fibre-reinforced epoxy this study highlights non-negligible porosity content (see Figure 10 and Table 1). Voids are located in the region of the 90° weft fibres which maintain the 0° fibres
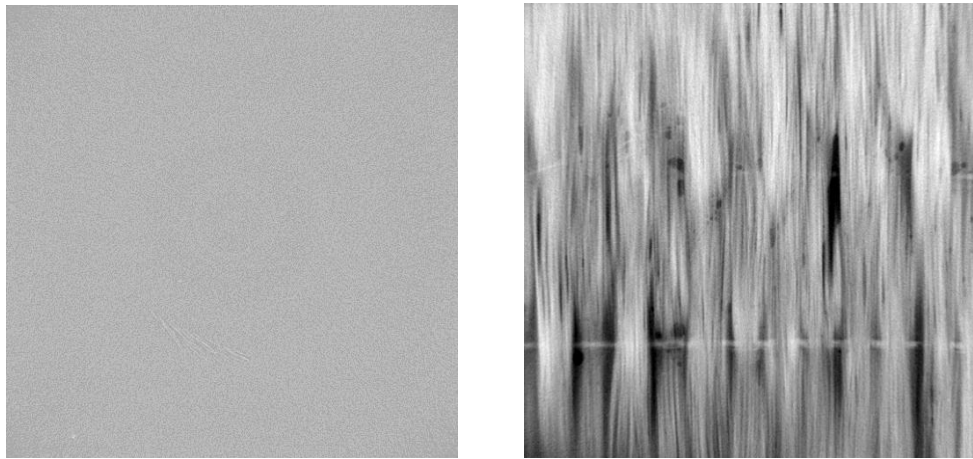
Figure 10: Examples of tomographic images of a resin specimen (left) and a composite specimen (right) at the same scale (25mm x 25mm)

Pressure	Specimen	Porosity (%)
1 bar	1	**5,95**
	2	**4,67**
	3	**5,29**
	4	**4,83**
	5	**4,98**

Pressure	Specimen	Porosity (%)
50 bar	2	**5**
	3	**4,72**
	4	**8,1**
	5	**6,42**

Pressure	Specimen	Porosity (%)
500 bar	1	**4,47**
	2	**4,58**
	3	**4,93**
	4	**5,46**
	5	**4,44**
	6	**4,23**

Table 1: Porosity ratio for each specimen

Since glass fibres are considered as a hydrophobic medium, water diffusion in the composite only takes place in the resin. This assumption results in lower moisture content in composites than in neat resin. Experimental values verify 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. 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 under any pressure. We can therefore make the hypothesis that additional water uptake in the composite is located in voids.

The weight of water uptake in the composite $\Delta Mglass\text{-}epoxy$ will be separated into the water weight in the resin $\Delta Mresin$ and the water weight in porosities $\Delta Mvoids$:

$$\Delta M_{glass-epoxy} = \Delta M_{voids} + \Delta M_{resin} \tag{9}$$

with:

$$\Delta M_{resin} = \frac{\Delta M_{resin}}{Mo_{resin}} \cdot Mo_{resin,composite} = C(t)_{resin}.Mo_{resin,glass-epoxy} \tag{10}$$

$$\Delta M_{glass-epoxy} = C(t)_{glass-epoxy}.Mo_{glass-epoxy} \tag{11}$$

Where $Mo_{resin,glass-epoxy}$ is the initial weight of resin in the composite.
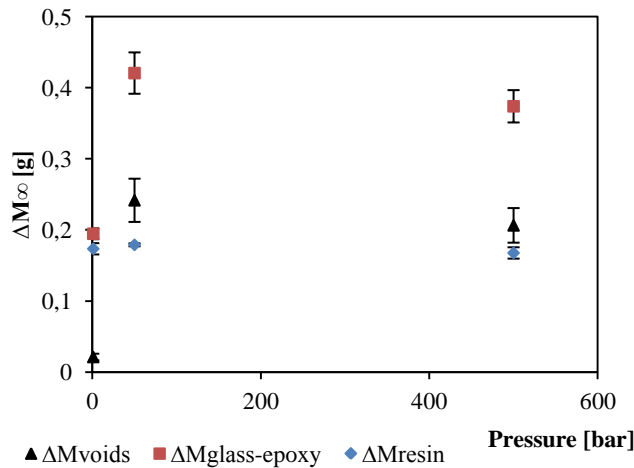

Figure 11: Water weight after saturation in the different media vs. pressure

The decomposition of water weight in the composite shows that porosities do not influence the water diffusion at 1 bar. The rise of water content in the composite between 1 and 50 bar is exclusively due to water diffusion into voids. Moisture content remains unchanged for pressure above 50 bar.

Moreover, additional water uptake in the composite ($\Delta Mvoids$) shows a significant dependence on the porosity level established in Table 1 (figure 12). For atmospheric pressure the presence of voids does not influence water diffusion. As soon as pressure rises, water uptake increases in proportion to the porosity ratio.
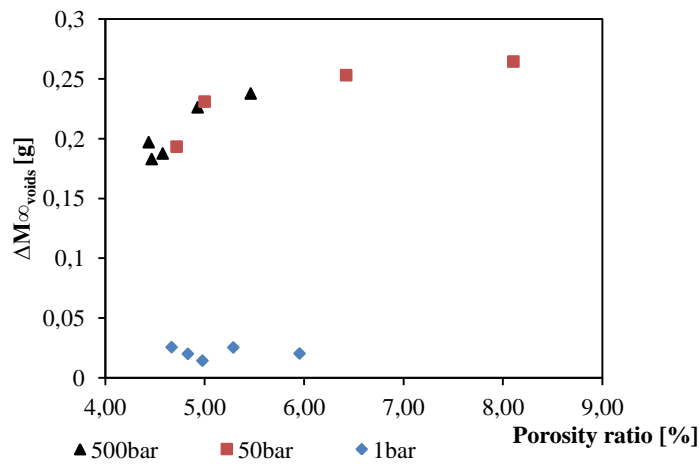
Figure 12: Water weight after saturation at different pressures vs. porosity ratio

5 CONCLUSION

An experimental study of weight gain by resin and 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 composite showed significantly higher weight gain under high pressure. The hypothesis was made that, based on microscopy and micro-tomography analyses, that 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.

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

ACKNOWLEDGEMENTS

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