CHARACTERIZATION OF SEA WATER AGEING EFFECTS ON MECHANICAL PROPERTIES OF CARBON/EPOXY COMPOSITES FOR TIDAL TURBINE BLADES.

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ABSTRACT

Composite materials are used in many marine structures and new applications are being developed such as tidal turbine blades. The reliability of these components, in a very severe environment, is crucial to the profitability of tidal current energy systems. These structures are subject to many forces such as ocean tides, waves, storms but also to various marine aggressions, such as sea water and corrosion. A thorough understanding of the fatigue behavior of the moving parts is therefore essential. The majority of tidal turbine developers have preferred carbon blades, so there is a need to understand how long immersion in the ocean affects these composites. In this study the long term behaviour of different carbon/epoxy composites has been studied using accelerated ageing tests. A significant reduction of composite strengths has been observed after saturation of the material in seawater. For longer immersions only small further changes in these properties occur. No significant changes have been observed for moduli nor for composite toughness. Changes in properties are initially due to matrix plasticisation, which increases failure strain, followed by reductions due to fibre/matrix interface changes. The evolution of the rate of water ingress into composite materials is important to follow, in order to develop predictive models of property changes through the laminate as a function of diffusion kinetics.

1 INTRODUCTION

Over the last 50 years composite materials have found many applications in the maritime domain, particularly in the yachting and offshore energy industries [1], [2]. Composite materials are used in many offshore structures and new applications are being developed such as tidal turbine blades. Tidal turbines offer an exciting opportunity to exploit ocean current flows to generate energy. The interest in the use of composite materials for tidal energy convertor structures is based on the potential improvements in hydrodynamic and structural performance. The reliability of these components, in a very severe environment, is crucial to the profitability of tidal current energy systems. These structures are subject to many forces such as ocean tides, waves, storms but also to various marine aggressions, such as sea water and corrosion. A thorough understanding of the fatigue behaviour of the moving parts (the turbine blades for example) is therefore essential. A previous study [3], [4], has highlighted the sensitivity of durability to the choice of components (fibre, resin, surface treatment of fibres). That work was carried out on thin composites reinforced by glass fibres. However, the majority of tidal turbine developers have preferred carbon fibre reinforced blades and the composite thicknesses are very large, especially in the area of connection between blade and hub. Under these conditions, sea water can induce changes in carbon/epoxy composite materials [5], [6]. The absorption of water molecules in polymer composites is known to have important effects on their final performance, especially in their long-term exploitation. By the organic nature of the matrix resin, often an epoxy, long immersion in sea water can induce both physical and chemical changes [7]. Swelling and plasticization are the main physical consequences of water absorption on polymer structures, while hydrolysis may be also be a concern. When composites are immersed at sea, water is first absorbed at the surface and then diffuses into the material. Some analogies between heat transfer and mass diffusion were established by Fick [8] in order to determine the kinetics of water entry into composites. Experimentally it is also possible to measure the evolution of water concentration in polymer and composite materials. There are various experimental methods but the simplest and definitely the most popular is based on sample weight measurements in the dry state (w_0) then in wet (w) conditions throughout the immersion time of the samples. Then it is possible to determine the water mass fraction: $m = (w - w_0) / w_0$ and quantify the diffusion behaviour of water in a composite material. Sea water ageing in the tidal turbine environment, at ocean temperature, will generate a slow process of degradation and damage in composites. Therefore there is a need to develop a procedure to accelerate ageing in order to assess the long term in-service behaviour of composites to be used in the marine environment. As a 25-year lifetime requirement is commonly specified in the renewable marine energy industry, the accelerated test protocol must aim to reproduce the effects of 25 years exposure in a few months [9].

The purpose of this paper is to characterise and model the effect of sea water diffusion on composite carbon/epoxy for tidal turbines blades. First, the characterization of the carbon/epoxy composites will be presented using standardized tests after different sea water ageing times. For this characterization, the sea water ageing process has been accelerated through immersion at higher temperature than ocean conditions. Second, a diffusion model taking into account the anisotropic nature of composite materials will be discussed.

2 MATERIALS AND METHODS

2.1 Materials

Tidal turbine blades could be manufactured using different processes and different materials, thus three processes and materials have been chosen:

A carbon reinforced epoxy pre-preg manufactured using the autoclave process, as this pre-preg could be used in blade spars. The samples were produced by FMC Composites in Brest. The UD pre-preg layers are composed of HexPly® M21 matrix and UD HexTow® IMA carbon fibers. Pre-preg curing conditions were respected following product data specifications. Full vacuum was applied on composites, followed by a 7 bar autoclave pressure at 180°C for 120 minutes.

A carbon reinforced epoxy made by resin transfer moulding (RTM), provided by Airborne Marine. The RTM material could be used in the blade body and blade spar elements. Airborne has already used the RTM process to manufacture one shot tidal turbine blades.

A carbon reinforced epoxy manufactured by vacuum infusion, this material could be used to manufacture the blade body. This carbon epoxy was manufactured in the LBMS Laboratory in Brest, using Tenax-E IMS65 carbon and the same epoxy resin as the RTM material. The samples were made on a glass plate, with a vacuum of 0.95 bars for the infusion process. All the plates were cured at 65°C for 16 hours.

This choice of material reflects the different current possibilities for manufacturing tidal turbine blades. It also allows the impact of fibre, matrix, and interface on the ageing mechanisms to be studied. Some details about the material composition are presented in Table1. It is worth mentioning that RTM and Infused materials were manufactured with the same epoxy resin, thus specimens of neat resin were also prepared to be studied. For this study, composite materials were produced with different orientations and thicknesses.

Materials	Process	Resin	Fibre
Infused	Infusion	Infusion/RTM resin	Tenax-E IMS*
RTM	RTM low pressure	Infusion/RTM resin	not available
Pre-preg	Autoclave 7 bar	Hexcel M21	IMA

Table1: Materials, process, resin and fibre compositions, (*IMS: intermediate modulus).

2.2 Accelerated sea water ageing procedure

The aim of an accelerated sea water ageing test method is to accelerate the mechanisms occurring in the normal marine environment and decrease the time to degrade a given material. For sea water ageing, the principal mechanism inducing degradation is the diffusion of water into the material. In an ocean environment the time process can be slow. As a consequence this ageing phenomenon must be accelerated to achieve an acceptable experimental time.

For this study different sea water baths at 25, 40, 60 and 80°C were used to characterize the diffusion of water into the studied materials. These baths, developed by Ifremer, allow materials to be aged at different temperatures in continuously renewed natural sea water directly pumped from the Brest Estuary. In order to accelerate the ageing process here, the RTM and the Infused materials were aged at 60°C, which is 15°C below their dry Tg. For the Pre-preg materials as the Tg is about 195°C it was possible to age at higher temperature, so this material was aged at 80°C. The Table 2 summarises the different Tg values and chosen aging temperatures for each material.

Materials		Tg	Ageing Temperature
Infused	[°C]	75 (1.4)	60
RTM	[°C]	77 (2.0)	60
Pre-preg	[°C]	195 (2.1)	80

Table 2: Comparison between Tg values and temperatures for accelerated ageing, mean (standard deviation).

Mechanical properties were characterized after three ageing times: T0 corresponds to the as-received material, T1 the time necessary to saturate the material in seawater. T2 and T3 are respectively equal to T1+1 and T1+2 months. More details about this ageing procedure can be found in [10].

2.3 Characterization of water diffusion into composites

Water uptake can affect the static characteristics, so in order to develop predictive models of property changes or water diffusion through the laminate the diffusion kinetics must be quantified, e.g.[11]. Sea water ageing was performed on each material at different temperatures. Specimens of each material with different thicknesses and material orientations were cut from composite plates by high pressure water jet cutting in the following dimensions, (3 specimens per condition of 50 x 50 x thickness mm^3). Then those samples were measured and weighed and finally distributed in four circulating natural sea water tanks at different temperatures: 25, 40, 60 and 80°C. Temperature is continuously monitored and controlled to ±1.5°C. Based on regular weight measurements made during ageing the water uptake was determined as a percentage of the initial weights of specimens.

2.4 Characterization of mechanical properties

The characterization of the elastic properties was performed using tensile tests on 90° and 0° laminates at a crosshead displacement rate of 2 mm/min, according to ISO 527, before and during sea water ageing. For the determination of mode I fracture toughness, DCB (Double Cantilever Beam) specimens were used in accordance with ISO 15024. The loading was introduced through bonded aluminium tabs. An electro-mechanical testing machine was used to load at a constant displacement rate of 1mm/min, all tests were filmed to follow crack propagation. Interlaminar Shear Stress (ILSS) tests were also used to follow the evolution of interfacial adhesion during ageing, according to EN ISO 14130. Tensile tests were performed on unreinforced dumbbell specimens at 2 mm/minute.

At least three specimens of each material per condition per test type were prepared and tested in the wet state.

3 RESULTS

3.1 Sea water diffusion in different composites

Examples of mean weight gain plots versus the square root of immersion time at 25°C, 40°C, 60°C and 80°C, are shown in Figure 1 (a) for the pure epoxy resin samples. The composite materials of the study have been immersed for 8000 hours. The diffusion kinetics of the materials can be fitted to a Fickian law. For each material, a stable weight gain is noted, after about 900 hours at 60°C for infused material, 1600 hours at 80°C for pre-preg and 2400 hours at 60°C for the RTM material.

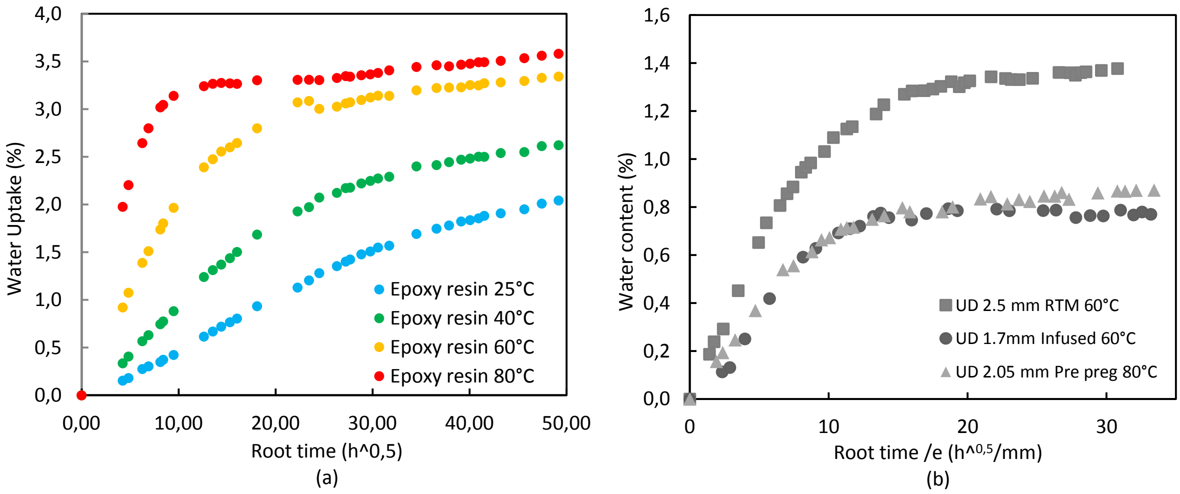


Figure 1: Plots of mean measured weight gains for pure epoxy resin (a), RTM and Infused 60°C and Pre-preg composites at 80°C (b).

Figure 1(b), presents some results of water uptake measurement for the three composite materials (only UD orientation). As tidal turbine blades could be manufactured using thick carbon epoxy laminates, it was important to compare the influence of the thickness and material orientation on sea water diffusion. Investigations presented in a previous study [10], highlight that diffusion kinetics and rate of water uptake are independent of the thickness of the composite. It was shown that water diffusion parameters are not influenced by the geometry of the specimen, suggesting that it is the through-thickness diffusion (D_x) which is dominating under these conditions.

3.2 Effect of sea water ageing on mechanical properties

For the three composite materials, a characterization of the mechanical properties was performed with tensile tests on specimens cut from UD panels at 90° and 0° after saturation. Three samples were tested in the wet state at 20°C for each condition (specimen dimensions 25 x 250 x thickness mm^3, following ISO 527 specifications), all cut using a high pressure water jet. Water uptake does not affect modulus, Figure 2, but has a particularly large effect on strengths, Figure 3. This is first due to matrix plasticization [7], which increases failure strain, followed by reductions due to both matrix and fibre/matrix interface changes.

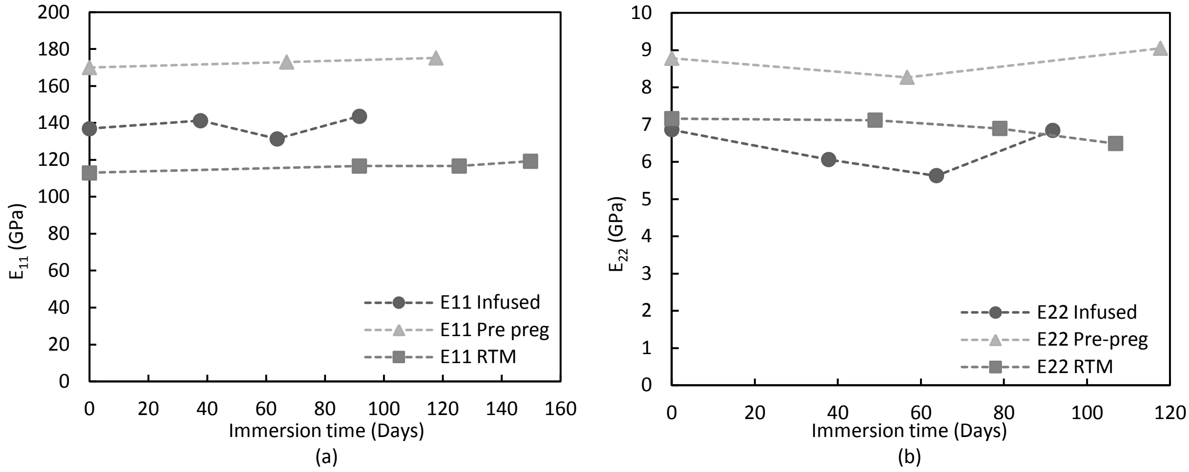


Figure 2: Plots of the evolution of mean longitudinal (E_{11}) (a) and transverse (E_{22}) (b) moduli for the three materials during accelerated sea water ageing at 60°C.

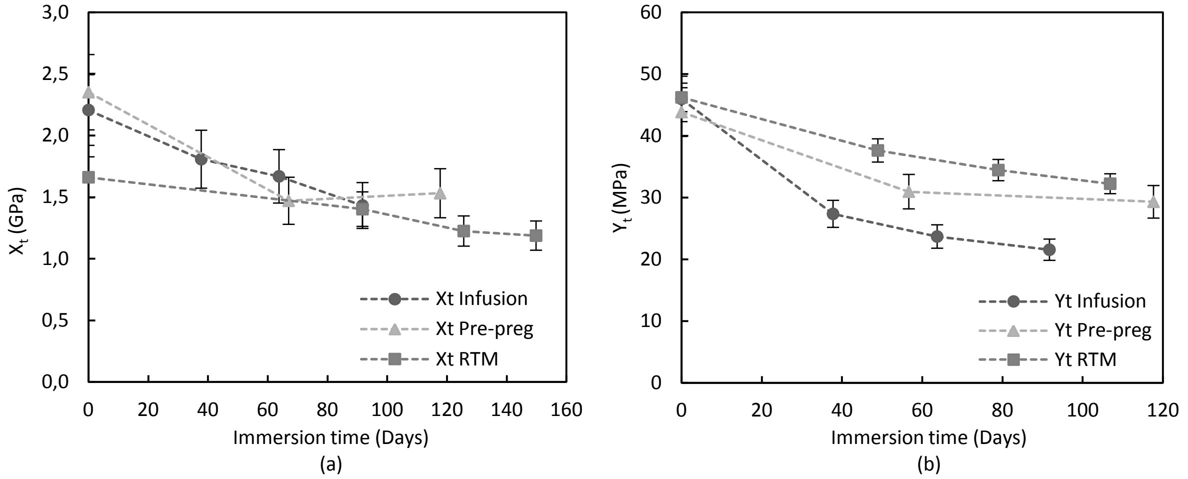
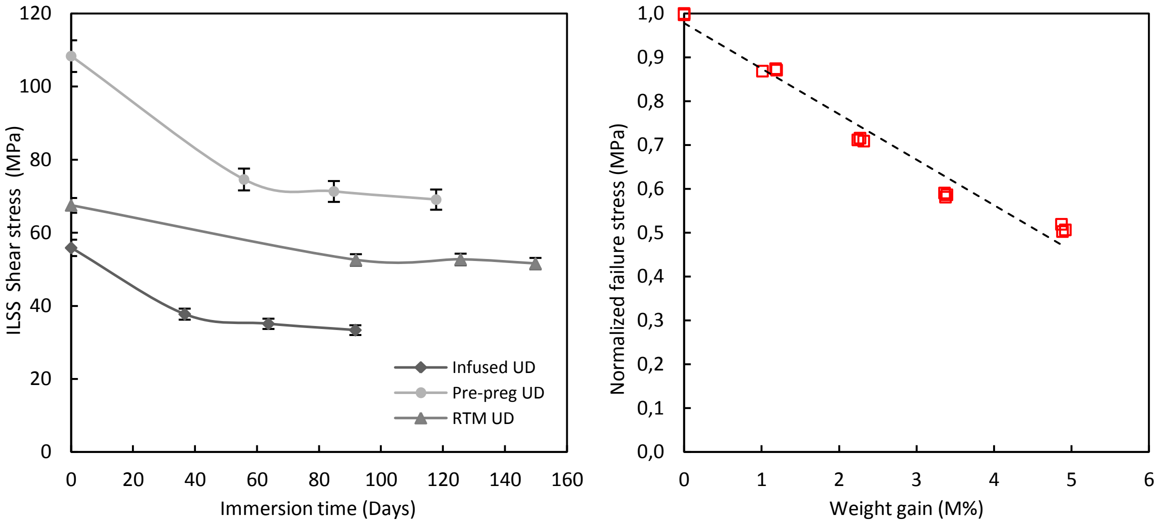


Figure 3: Plots of the evolution of mean longitudinal (X_t) (a) and transverse (Y_t) (b) tensile strengths for the three materials during accelerated sea water ageing at 60°C. Scatter bars show standard deviations.

ILSS tests are often used for monitoring quality and are suitable for the comparison of materials. These tests provide information about the quality of the resin-fibre bond. The evolution of the interlaminar shear stress during ageing has been followed for different material orientations and thicknesses.

As shown in Figure 4a, the decrease of interlaminar shear stress in both cases is quite large, about 20-30% for these UD materials. A parallel study on unreinforced resin, Figure 4b, also shows a significant drop in tensile strength after saturation, so both mechanisms participate during sea water ageing.



(a) (b)

Figure 4: (a) Changes in mean ILSS shear stress strength during sea water ageing at 60°C for three different UD materials. Scatter bars show standard deviations, (b) Tensile strength of unreinforced resin at different conditions up to saturation (4.8% weight gain).

The evolution of composite materials' toughness has been investigated using DCB tests during ageing. DCB tests were performed on unaged material, then after three different ageing times. The effect of water ageing on the toughness is quite limited, as shown in Figure 5.

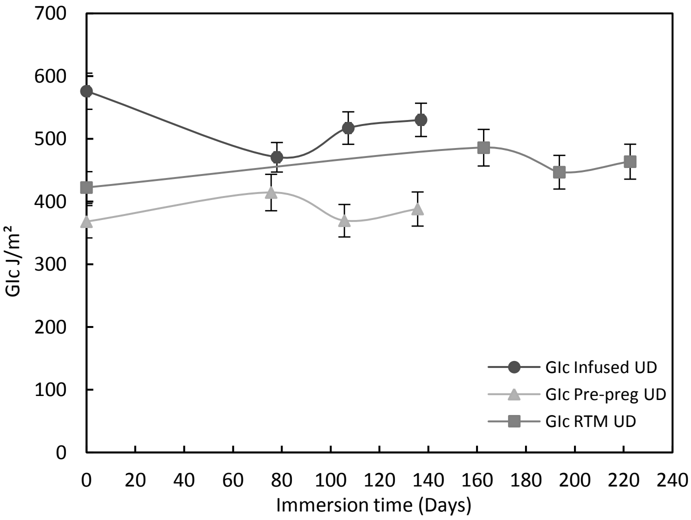


Figure 5: Evolution of critical strain energy release rate G_{Ic} in carbon/epoxy Pre-preg, Infused and RTM materials during sea water ageing.

4 MODELLING OF SEA WATER DIFFUSION IN COMPOSITES

4.1 Model presentation

Water uptake measurements reflect global diffusion properties. To account for the anisotropic nature of these composite materials, a model of diffusion based on a finite element analysis using Abaqus™ was developed, in order to determine diffusion coefficients in the three material directions.

The objectives of the model are to be simple to use and to be applicable to large structures such as tidal turbine blades.

According to the work of Shen and Springer [8], it is possible to define diffusion parameters for unidirectional composites. The diffusivity D_x is the water diffusion coefficient for a material composite in the direction normal to the surface. It can be numerically determined. For composite materials reinforced by fibres the coefficients of diffusion $D_{x,}$, D_y and D_z can be determined using three parameters:

- The Diffusion coefficient of the resin D_r,
- The Diffusion coefficient of the fibres D_f,
- The volume fraction of fibres V_f,

In the case of an unidirectional material, it is assumed that $D_{x,}= D_y$, which are the diffusion coefficients transverse to the fibres, and D_z is the coefficient along the fibres

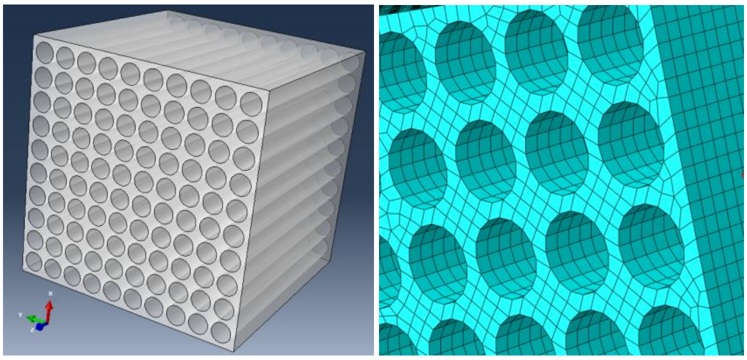
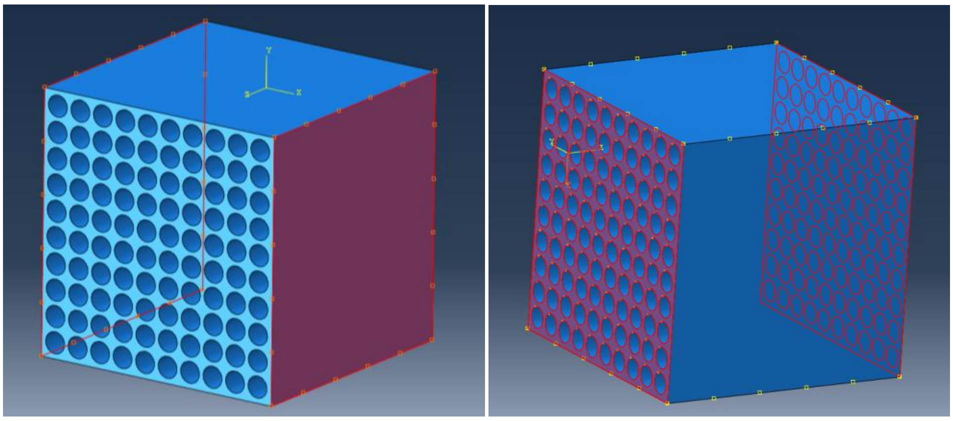

(a) (b)

Figure 6: (a) Representation of the 3D model using for diffusion in Abaqus™ and (b) the associated mesh.

Using Abaqus™ and entering the water diffusion coefficient, density, specific heat of the matrix and the composite fibre fraction, it is possible to determine for an UD laminate the diffusion through the thickness and in the fibre direction. In the specific case of carbon/epoxy we will consider that carbon fibres do not participate in water diffusion.

In this 3D model an elementary geometry can be defined using composites parameters, volume fraction of fibres and diameter of carbon fibres, as presented in Figure 6 (a). We assume that this geometry reflects a global fibre content and a perfect fibre distribution with a tetragonal arrangement. To reduce computation time, the size of the geometry is limited to a 60x60x60µm^3 volume (with fibres of 5 or 7µm diameter). The sensitivity of the mesh was studied and then an optimal mesh size was chosen as 1µm with hex elements, as shown in Figure 6 (b).

In order to determine diffusion coefficients in the longitudinal and transverse direction to fibres, two different cases of simulation were performed. In the first case, boundary conditions of diffusion were applied to the parallel surfaces of the cube, as shown on Figure 7 (a). In this case diffusion will occur perpendicular to fibres. In the second case, the water concentration was applied to the surfaces perpendicular to the fibres, as presented in Figure 7 (b).



(a) (b)

Figure 7: Representation of boundary conditions applied on the 3D model for transverse (a) and longitudinal (b) diffusion thought composite.

The post processing of the FE calculation was performed with a Python script. This script averages the concentration water for the whole model at each time step (to simulate the gravimetric measurement of sea water diffusion in composite samples). Thus the global evolution of water concentration is plotted as a function of the square root of time normalized by the thickness.

Parameters		Epoxy resin 60°C	M21 resin 70°C
D_r	$[10E^{-13}\ m^2.s^{-1}]$	13.4	4.5[13]
ρ_r	$[Kg.m^3]$	1168	1280[13]
C_r	$[J.Kg^{-1}.C^{-1}]$	1800	1800

Table 3: Model parameters based on experimental measurements at 60°C in sea water and from literature at 70°C in deionised water.

For the simulation of the diffusion into different composites, the parameters of the model were either determined experimentally or taken from the literature, as presented on Table 3. For each composite material an estimation of the fibre content was obtained by pycnometry measurement. Thus the carbon fibre contents in RTM, Infused and Pre-preg materials, are respectively 50, 54 and 58%.

4.2 Results and validation of the model

In the following section different FE simulations will be presented and compared to the experimental results presented previously. These simulations were run for the same temperatures as those used to age the materials to determine the evolution of the mechanical properties. For the Pre-preg material (IMAM21), it was not possible to determine experimentally the diffusion coefficient of the resin, due the difficulty to obtain the unreinforced M21 matrix resin, but from a previous study [13], we obtained the diffusion coefficient at 70°C in deionised water. The ageing in deionized water is considered to be more aggressive than sea water, but this diffusivity will be used in order to compare the model with the Pre-preg experimental results for sea water diffusion at 60°C and 80°C.

In Figure 8 and Figure 9, the FE model of diffusion in the perpendicular direction to the fibres is compared to composite experimental results.

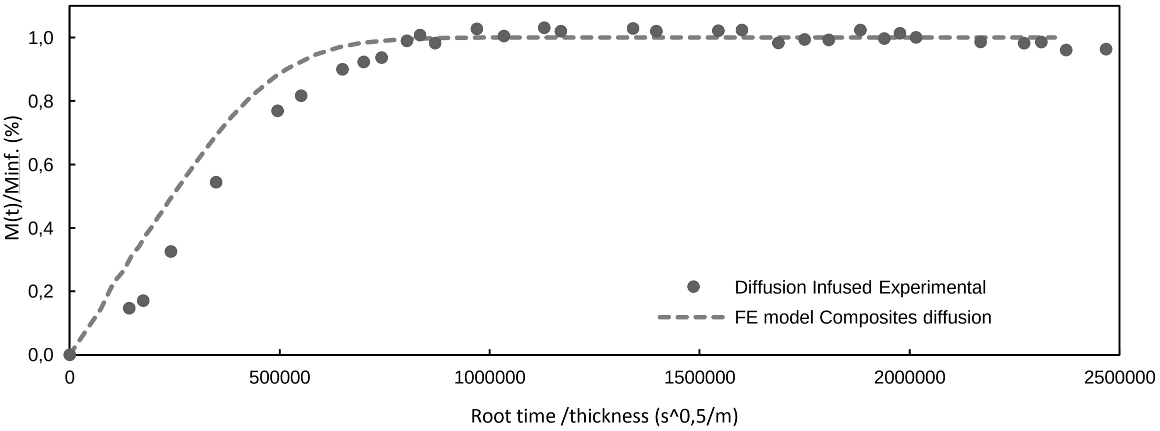


Figure 8: Comparison between FE model (diffusion in transverse direction) and experimental results for the Infused UD at 60°C.

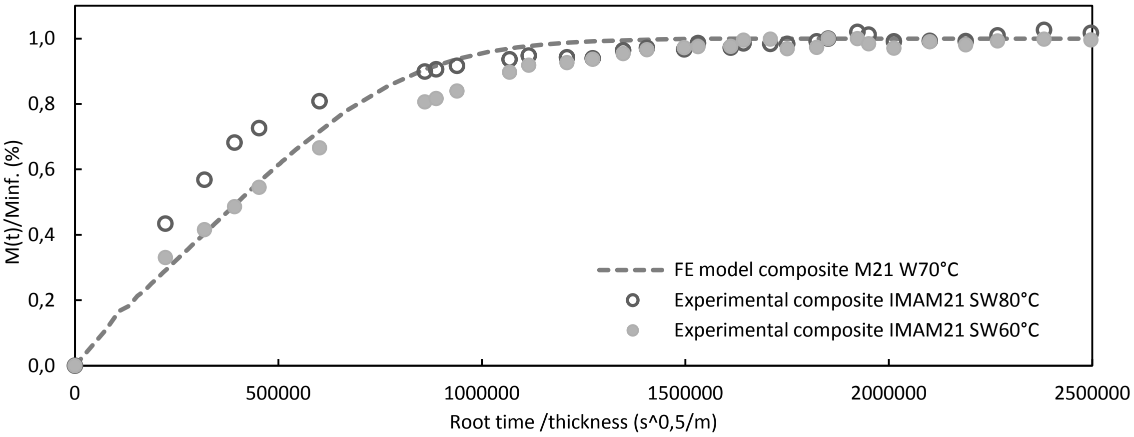


Figure 9: Comparison between FE model (diffusion in transverse direction at 70°C) and experimental results for the UD Pre-preg at 60°C and 80°C.

A good correlation between FE model results and diffusion tests has been found for the Infused composite, as shown in Figure 8, but the the model slightly overestimates the diffusion kinetics. This phenomenon could be explained by the organisation of the fibres in the 3D model. If the fibres were randomly organised the water diffusion through the matrix would be slower. The results presented in Figure 9 also show a reasonable estimation of the kinetics of diffusion at 70°C despite the fact that in this case the model prediction is compared to experimental results for sea water diffusion at 60°C and 80°C.

Based on the diffusion plots of each material, it is possible to identify water diffusion coefficients D_x and D_z. These diffusivities were obtained using the Fickian law. The slope a of diffusion plots allow D_x and D_z to be determined as presented in equation (3). (M_t/M_{inf} is the ratio between the total mass of water absorbed at a time t and the maximum mass of water at equilibrium).

$$D = \frac{\pi}{16} a^2 \tag{3}$$

Table 4 presents the different coefficients obtained with the model in the normal and parallel directions to the fibres for three different materials. These model results are compared to theoretical and experimental diffusion coefficients. The theoretical coefficients are determined as described in

[8]. Water diffusion coefficients identified with the model are in accordance with the experimental ones. As discussed previously, the model slightly over estimates diffusion coefficients due to the fibre arrangement on the 3D geometry. However as seen on Figure 8, the diffusion kinetics curves are close**.** It is worth mentioning that the effect of fibre contents on water diffusion is taken into account correctly by the model. For instance, RTM material (V_f=50%) shows higher diffusion coefficients than the Infused composite (V_f=54%).

Water diffusion coefficient	[10^{-13} m².s^{-1}]	Infused 60°C	RTM 60°C	Pre-preg 70°C
Theory D_x		2.28	2.70	0.63
Theory D_z		6.16	6.70	1.89
Model D_x		**7.23**	**7.92**	**2.84**
Model D_z		10.9	11.49	4.39
Experimental D_x		**4.48**	**5.08**	**2.54*-5.43****

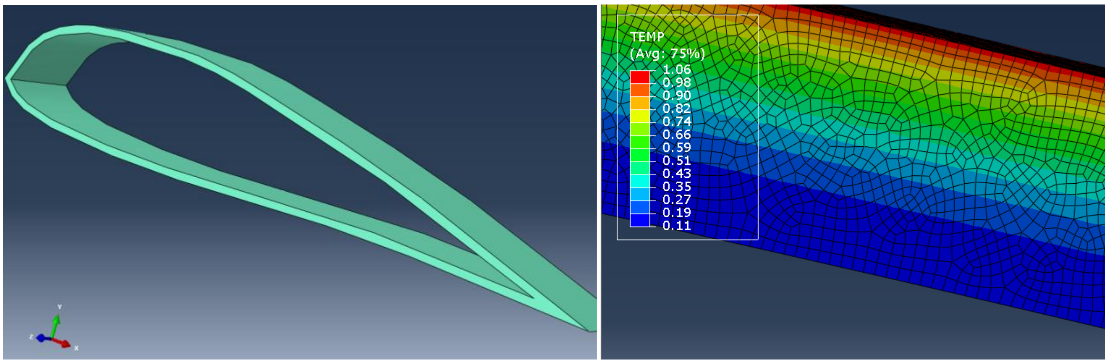
Table 4: Comparison between theoretical, model simulation and experimental water diffusion coefficients. (*experimental Pre-preg at 60°C ** experimental Pre-preg at 80°C).

These water diffusion coefficients D_x and D_z can now be determined at the lower temperatures reflecting the underwater environment, and used to analyze larger structures with different stacking sequences.

4.3 Application to a large blade structure

A first study of sea water diffusion in a large tidal turbine blade structure has been performed using the method presented above. The aim was to have a first estimation of the long term water diffusion into a large structure. As sea water ageing has important effects on mechanical properties, it is necessary to estimate the sea water entry in such structures.

Thus a 3D blade model was used. This model is presented solely as an example, it does not represent a particular blade. For this 3D geometry, only a short section was considered (100 mm). The average dimensions of this section are 1000 mm by 200 mm and the thickness of the composite skin is 20 mm. An illustration of the blade section is presented in Figure 10 (a). The boundary conditions of the diffusion were only applied on the outer composite skin of the blade with the composite diffusivity determined at 25°C.



(a) (b)

Figure 10: Illustration of the 3D geometry of the blade model (a) and the local diffusion of water in the blade trailing edge (b) after 25 years of immersion at 25°C.

The water diffusion results in the blade section are presented in Figure 11. The service life of tidal turbines is given by some manufacturers as 25 years. For this immersion time the model estimates that the composites of the blade reach an average concentration of water of 0.8 (for this geometry and thickness). So after 25 years of immersion the 20mm thick blade will not be fully saturated by the seawater, but some outer composite layers will be fully saturated, as shown in Figure 10 (b). For instance 8% of the thickness of the blade is fully saturated after 25 years. And 15% of this thickness has a water content between 90% and 65%. In these composite layers a weakening of the mechanical properties between 20-40% will appear, as presented in Figure 3 and 4.

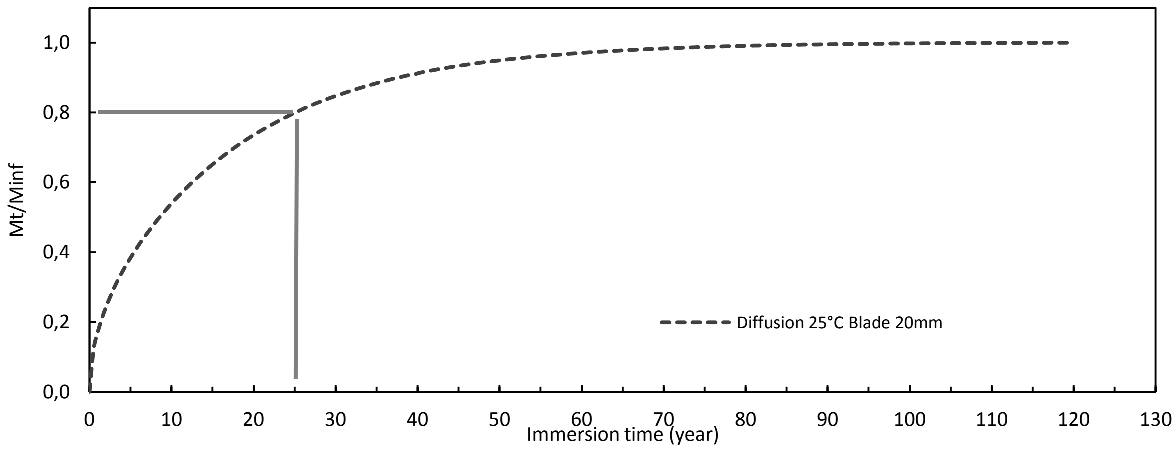


Figure 11: Evolution of the diffusion of water at 25°C in the blade model as a function of the immersion time in years.

5 CONCLUSION

Water uptake has a particularly severe effect on the static characteristics of certain carbon/epoxy composites proposed for tidal turbine blades. The evolution of the rate of water entry into different composite materials and epoxy resin has been quantified, in order to develop predictive models of sea water diffusion through the laminate. Using standardized tests on composites with different orientations, the effect of sea water ageing was evaluated, and after the first ageing period a decrease of 20% to 40% in failure strengths but minimal changes in elastic moduli and toughness were observed. During sea water ageing, an important weakening of both the resin and the interface between fibres and matrix has been revealed. As composites are more and more frequently used for tidal turbine applications, it is important to model and predict the long term diffusion of water. In a first step a simple finite element model was developed in order to determine the diffusion characteristics, using simple physical parameters. In a second step diffusion coefficients were used to predict long term diffusion in a blade model section. The results reveal that after 25 years the composites is not fully saturated in water, but layers are fully saturated close to the water exposed side. As a consequence mechanical integrity of these layers could be compromised. It is important to mention that the diffusion kinetics depend on the geometry of the structure (e.g. thickness), so for thicker structure the time for water to reach its maximum concentration will be extended. However some factors can aggravate and accelerate the diffusion process in a tidal turbine blade. High loading, fatigue loading, and abrasion, may induce damage into the composite structure. This damage could induce cracks in composite layers which will create new pathways for water and as a consequence accelerate diffusion and ageing. Coupled diffusion/damage models should therefore be applied and these are currently being studied.

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