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Water diffusion in RTM textile composites for aircraft applications

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Abstract. This paper presents a first step towards the understanding of water diffusion in RTM textile composite materials for aircraft applications and focuses on the development of experimental and numerical approaches to characterize the diffusion kinetics within the material.

The method consists in making samples which are representative of the materials architecture and carrying out gravimetric tests on such samples. Analysis of results with the aid of a diffusion model reconstructing the architecture of the samples helps identifying the diffusion behaviour of the material.

Keywords: organic matrix composites; hygrothermal ageing; textile composites; thermosetting resins; RTM

1. Introduction

To allow weight reduction of aircraft structures, the employment of new materials (for instance CFRP) and new manufacturing processes (for instance RTM) is foreseen, in particular for warm temperature structural parts such as turboengines and nacelles. The certification of such structural parts must be done under realistic in-service conditions, in particular for harsh humid environments. It is well known that organic matrix composite materials are sensitive to humid ageing: in fact, water absorption-which takes place by means of chemical mechanisms (bonding of the water molecules with the macromolecules of the organic phase of the composite)-may promote consistent changes of the mechanical properties of the composite material (Weitsman 2012). Since water diffusion by chemical mechanisms is relatively slow (compared for instance to thermal diffusion or water penetration on pores/cracks by capillarity), species (or bonds) concentration gradients are likely to develop, therefore degradation phenomena take place at a local scale, which is usually microscopic, depending on the extent of the gradient (Weitsman 2000, 2012, Merdas *et*

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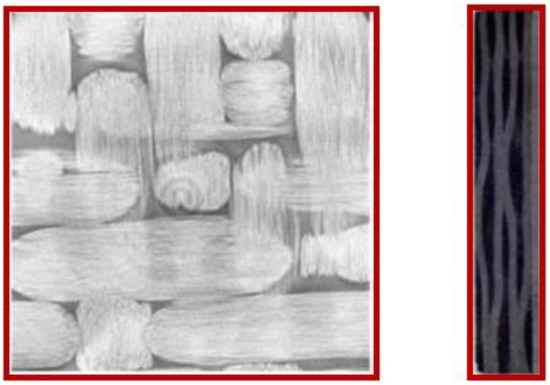

Fig. 1 Example of material with complex microstructure

al. 2002).

Despite the consistent development of experimental methods (infra-red spectroscopy and nuclear magnetic resonance) for detecting bound water molecules in polymers (De'Nève *et al.* 1993, Mensitieri *et al.* 1995, 2006, Popineau *et al.* 2005), it is not possible to quantitatively measure water concentration in composite samples: therefore, in order to estimate water concentration (and property) profiles in materials and structures, it is essential to perform numerical simulations: within the context of industrial applications, the classical Fick's model (the equivalent of Fourier's model for thermal conduction) is often appropriate since diffusion anomalies (departure from Fickian behaviour) are not much marked or visible only after long exposure times (Crank 1975, Weitsman 2000, 2012).

In order to characterize the diffusion behavior in complex materials, in particular for materials with a complex microstructure (Fig. 1), two strategies can be employed: the first one foresees the employment of "equivalent" homogeneous medium models (Beringhier and Gigliotti 2015, Beringhier *et al.* 2016, Gigliotti and Jacquemin 2013, Grace and Altan 2012, Gurtin and Yatomi 1979, Pierron *et al.* 2002, Simar *et al.* 2014, Weitsman 2000, 2012), and involves studying the diffuso-mechanical behaviour of such materials by these models. This strategy is applicable and needed for structural simulations but not good for understanding diffusion mechanisms.

The second strategy consists in studying species diffusion within a repetitive tow pattern (see for instance, Tang *et al.* 2005), which is good for understanding of diffusion mechanisms at the microstructural level but not applicable for structural simulations. The present work aims at discussing models containing the explicit representation of the microstructure for understanding the diffusion behaviour of the textile material and the mechanisms of water diffusion within such material. In particular, the present work aims at predicting the diffusion behavior of a C/epoxy 2D 5 harness fabric textile material by the knowledge of the behavior of the resin material and by employing a realistic representation of an Elementary Repetitive Unit (5×5 tows), that is, the detail of the microstructure of the reinforcement textile phase.

The architecture of the reinforcement has a two-scale microstructure and characterized by the textured architecture of the 2D 5 harness fabric and the architecture of the tow (1 tow=several thousands of fibers, microscale).

In order to catch the two-scale effect, two sets of tests are carried out:

-One set of tests at the mesoscopic scale, involving water sorption in one Elementary Representative Volume (ERP) of the materials,

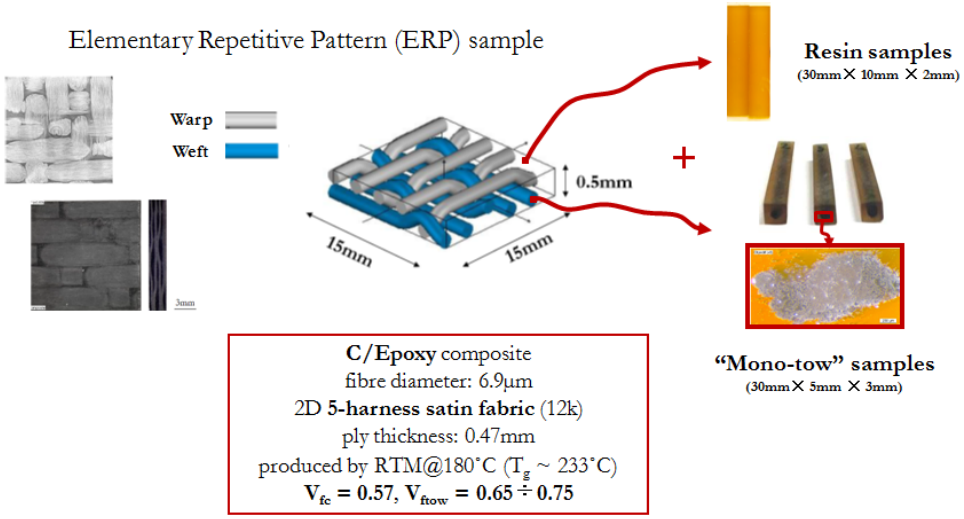

Fig. 2 Material system employed in the present study

-One set of tests at the microscopic scale, involving water sorption and ultra-micro indentation tests in a "single-tow" sample (a sample containing only one tow).

The paper is organized as follows: Section 2 presents the material, the experimental setup and tests, Section 3 illustrates the modelling and simulation results while Section 4 presents conclusions.

2. Material, experimental setup and tests

The material system is illustrated in Fig. 2. For the study of diffusion at the microstructural level we employ a sample containing one Elementary Repetitive Pattern (which we call ERP) of the material. The composite material is made by a epoxy matrix and a "high strength" carbon fibre manufactured by the same supplier: the fibre has circular section with a diameter of 6.9 μm. The preform employed to produce structural components is a 2D 5-harness satin fabric each tow containing 12000 filaments of carbon, 12K, powder-free, 500 g m^{-2} weight. The thickness of a ply is 0.47 mm. Additional characterization at the microstructural level is performed by employing pure resin samples and specifically developed "single-tow" samples, whose characteristics and dimensions are reported in Fig. 2, for characterizing the behavior of the elementary constituents of the material. For the study of diffusion at the macroscopic level we employ composite samples, for instance by taking samples which are multiple of a ERP. In any case we employ a C/epoxy material: the average total fibre volume fraction is 0.57 (established by burning the resin and measuring the fibre content); the fibre volume fraction in a tow (established by random optical micrographic observations on the ERP microstructure) is between 0.65 and 0.75.

The ERP sample presents several rich zones between tows and close to the external surfaces directly exposed to the environment, while the tows exhibit very high fibre volume fraction values. The tows are well compacted by the 5-harness satin configuration allows for quite high matrix volume fraction values around tows and close to the surfaces.

Gravimetric tests are performed by employing a high precision regulated SECASI climatic

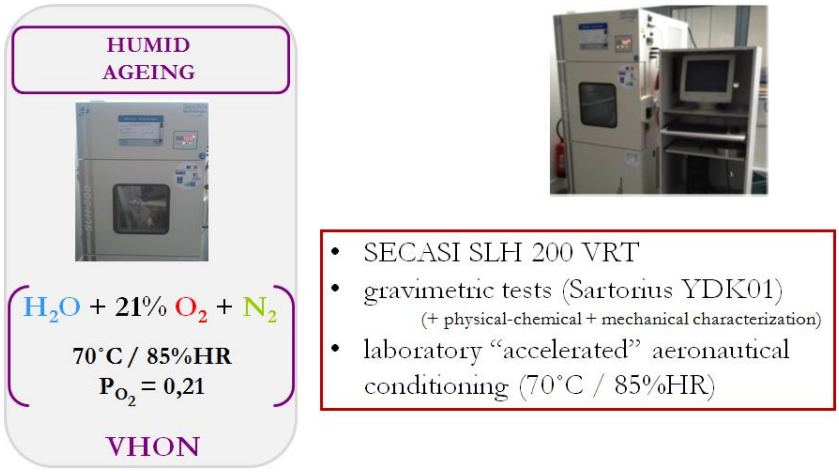

Fig. 3 Setup and equipment

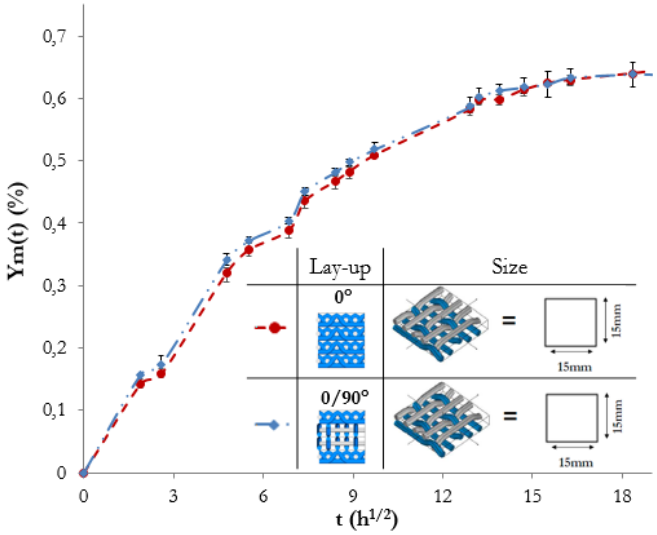

Fig. 4 Sorption curve for the ERP sample

chamber and a high precision Sartorius YDK01 balance (Fig. 3). The tested humid environment is representative of laboratory "accelerated" aeronautical conditioning (70°C and 85 % HR, referred as VHON environment, see Fig. 3).

Fig. 4 illustrates the result of a sorption test on a 4-ply ERP sample subjected to constant environmental conditions (T=70°C, HR=85%): the mass fraction, Ym(t) of the sample-defined as

$$Ym(t) = \frac{M(t) - M_0}{M_0} \tag{1}$$

in which M(t) is the sample mass at time t and M_0 is the initial sample mass-is represented as a function of (square root of) time.

The behavior of the composite is approximately Fickian, linear with square root of time and

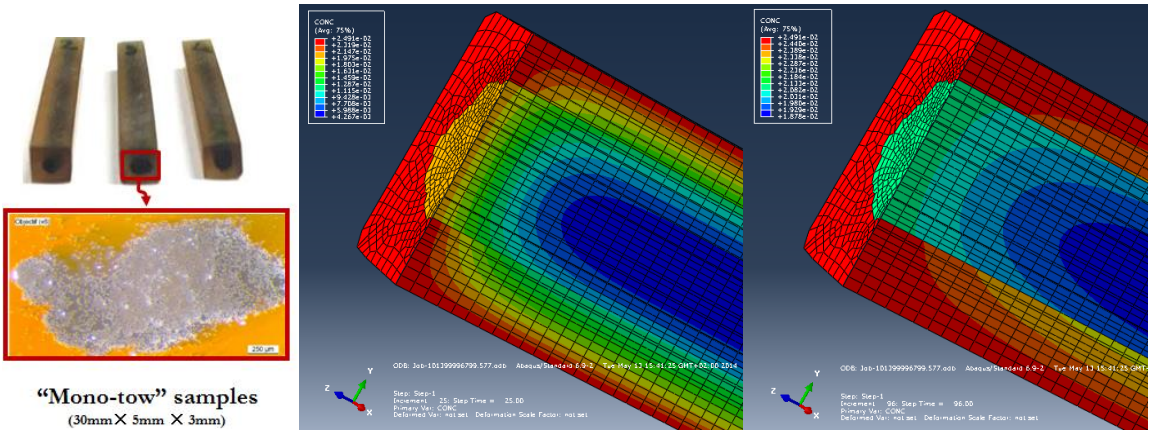

Fig. 5 "Single-tow" samples and sorption test numerical model

showing pseudo-saturation, qualitatively similar to that of the pure resin explored in a precedent paper (Simar *et al.* 2014). In the case of the pure resin, departure from pure Fickian behaviour is observed after long exposure time, this is due to the occurrence of thermo-oxidation reaction-diffusion phenomena taking place simultaneously with pure water diffusion. This behaviour has been extensively described and discussed in (Simar *et al.* 2014) for the pure resin. This behaviour is not observed for the composite samples, at least for the considered conditioning time, moreover in the present case the diffusion anomalies observed in the pure resin are mitigated by the presence of fibres.

Fig. 5 illustrates the schematics of a sorption test carried out on the elementary constituents of the textile material, pure resin and "single-tow" samples-representing the diffusion behaviour of a single tow, together with the scheme of the adopted numerical simulations employing the Fick's model (Crank 1975). For the resin material isotropic behaviour is employed, with diffusivity constant, D_r, equal to 0.016 mm^2/h and saturation concentration, $c_{\infty r}$, equal to 2.49×10-5 g/mm^3. The Fickian resin properties of the resin were identified in the cited paper by (Simar *et al.* 2014). In the "single-tow" sample, since the carbon fibres are hydrophobic, the properties of the tow material can be assumed as orthotropic, with a diffusion property along the fibre direction, $D_{tow|}$, diffusivity in the direction transverse to the fibre, $D_{tow\perp}$, and a saturation concentration noted as $c_{\infty tow}$. These last properties can be found by employing analytical homogenisation formulas (such as for instance those proposed by Halpin and Kardos 1976, Shen and Springer 1976, Shirell and Halpin 1977). In the present paper we focus on the Halpin and Kardos formulas (Halpin and Kardos 1976), for which

$$D_{tow|} = D_r \tag{2}$$

$$D_{tow\perp} = D_r \frac{(1 - V_{ftow})}{(1 + V_{ftow})} \tag{3}$$

$$c_{\infty tow} = c_{\infty r}(1 - V_{ftow}) \tag{4}$$

in which V_{ftow} is the fibre volume fraction of the tow.

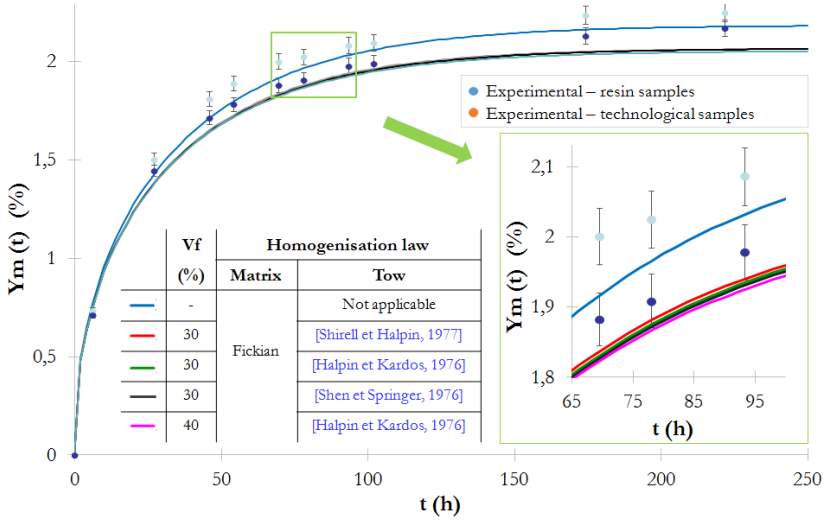

Fig. 6 Sorption curves for pure resin and "single-tow" samples (experimental vs. numerical)

At the "single-tow" sample boundary the following boundary condition is imposed

$$c_b = c_{\infty r} \quad \text{(on resin zones) or} \quad c_b = c_{\infty tow} \quad \text{(on tow zones)} \tag{5}$$

while at the interface between pure resin and tow material the following interface condition is imposed

$$\bar{c}_r = \bar{c}_{tow} \rightarrow \frac{c_r}{S_r} = \frac{c_{tow}}{S_{tow}} \tag{6}$$

stating that-at the resin/tow interface-the resin and tow normalized concentrations-defined as the actual concentration divided by the respective material solubility-are equal. The resin solubility-denoted by S_r-is taken equal to 1, while the tow solubility-denoted by S_{tow}-is equal to 1-V_{ftow}.

Fig. 6 illustrates the result of a sorption test for the "single-tow" sample, the comparison between the experimental test and the numerical simulations employing different homogenisation rules for the tow diffusivity coefficients.

It can be noted that there is good agreement between experimental and numerical simulated sorption tests. Incidentally, all analytical homogenisation formulas are suitable for a good simulation of the experimental curve. This is because-for the given tow fibre volume fraction value-these formulas are very close and give almost the same predictions. The result in Fig. 6 testifies that negiglible or no effects come from tow/resin interfaces, since the pure employment of models involving analytical homogenisation laws is sufficient for describing in reasonable manner the sorption curve. Fig. 7 illustrates the results of ultra micro indentation tests carried out on "single-tow" samples. Elastic Indentation Moduli (EIT) measurements are carried out following the Oliver and Pharr technique (for more details see, for instance, Minervino *et al.* 2013). Tests are performed at different heights (160 μm, 300 μm, 530 μm, sample centre) starting from the top sample surface (Fig. 6, left) on humid aged (VHON) samples and EIT values are reported as a function of the distance from the tow location (from left to right) and from the external edge location (from right to left).

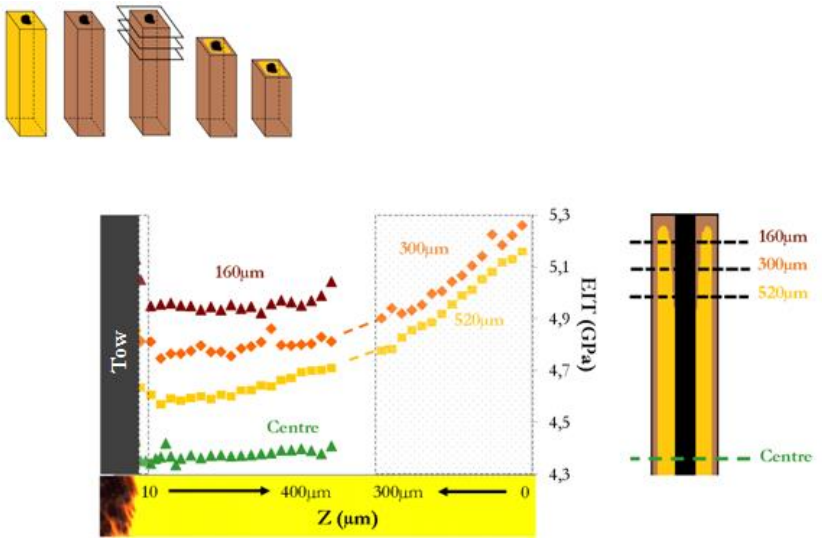

Fig. 7 UMI tests on "single-tow" samples

For all sample height values, EIT profiles suffer from gradients close to the external surfaces and to the tow/matrix interface. The small property gradients visible close to the external surface directly exposed to the environment are the trace of the irreversible thermo-oxidation phenomena taking place in the pure resin during sorption tests at 70°C (Simar *et al.* 2014): these effects are visible along a thermo-oxidized layer of some hundred of microns (around 300 μm in this case) and are correlated with colour changes in the same zones (the sample is darker close to the external surfaces). Gradients close to the tow/matrix interface are related to the presence of the tow, mainly mechanical constraining from the tow fibres, which are much stiffer than the matrix. An exact interpretation of this last phenomenon would need further investigation-currently under study-which is out of the scope of the present paper. Here we simply note that the intensity of gradients occurring close to the tow/matrix interface is never greater than those affecting the zone close to the external surface. This result is useful to conclude that no or negligible diffusion effect is coming from the tow/matrix interface zone: in fact, if this effect would be sensible, much greater gradients would be noted close to the tow/matrix interface than to the external surface-the presence interface would lead to preferential accelerated diffusion close to the tow materials. It can be concluded that-at least as far as the diffusion behaviour is concerned-none of such effects is visible, the influence of the tow/matrix interface can be considered as negligible.

3. Modelling and simulation results

Sorption modelling of the textile material is carried out by considering two distinct phases: the matrix, with isotropic behavior identified on pure resin samples; the behavior is hypothesized as Fickian since a saturated concentration value is employed. The fibrous tow with orthotropic behavior identified on "single-tow" samples. As for "single-tow" samples, we employ homogenized diffusion properties for the tow which is made of fibres and resin: in particular, the diffusion coefficient along fibres is taken equal to that of the resin: for the transverse diffusion

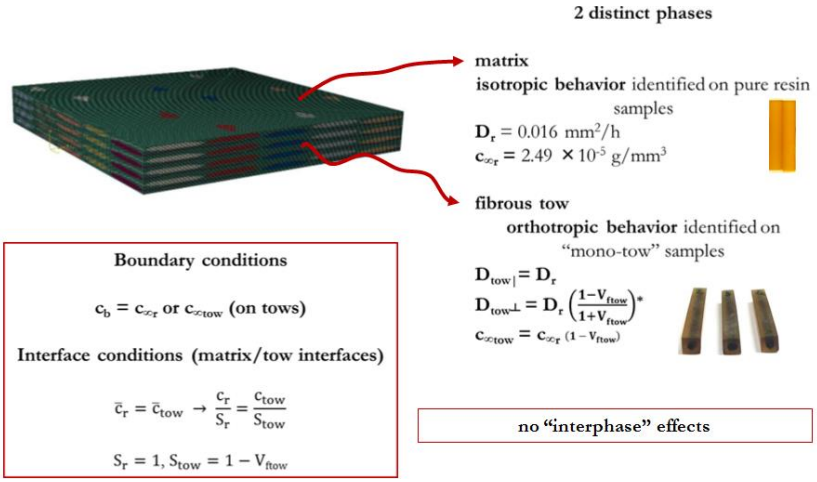

Fig. 8 Diffusion model in textile ERP composite

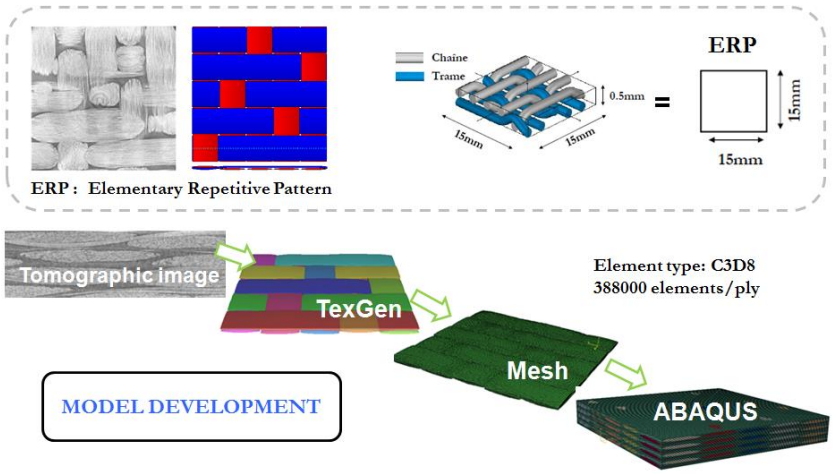

Fig. 9 Development of the FEM diffusion model

coefficient and the saturated concentration value of the tow simple homogenization formulas are employed. At the boundary, the imposed constant concentration is equal to the saturation concentration for resin or tows, at the interface between matrix and tows the adimensional concentrations or resin and tows-that is their true concentrations divided by their solubility values-are made equal. The additional hypothesis here is that there are no interface or interphase effects (see Fig. 8).

The model is developed in the ABAQUS commercial FEM software (Fig. 9), generated by a TEXGEN plot, which is an idealized model, but quite realistic, since it is built starting from µtomographic close observations of the microstructure (such as those in Fig. 1). Fig. 9 illustrates all the steps of model development: the µtomographic image of the microstructure (1 ERP, dimensions in Fig. 9) is employed for building a TEXGEN plot of the fibrous tow material architecture, which is then meshed in ABAQUS. The matrix material is add in a further step. Then the full model is meshed by the ABAQUS structured mesher. 388000 C3D8 solid elements per ply

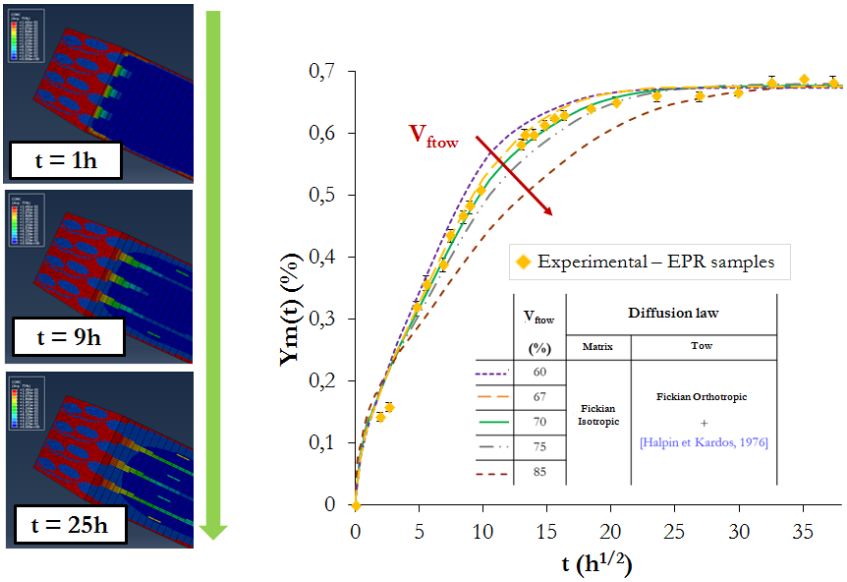

Fig. 10 Concentration and water mass evolution with conditioning time: Numerical vs. Experimental

and the MASS DIFFUSION solver are employed for diffusion simulations.

Fig. 10 illustrates concentration and water mass evolution in the ERP textile sample as a function of time for different values of the fibre tow volume fraction. For the sample mass a comparison between the numerical and the experimental result is provided. Water concentration charts (only numerical) help understanding where water diffuses within the textile material; as expected, diffusion takes place primarily in matrix rich zones and slows down in tow material. This kind of information is important since no experimental techniques are currently available for measuring water concentration full fields within a polymeric material.

Several conclusions can be drawn from Fig. 10, in particular for what concerns water mass absorption (right in Fig. 10), directly comparable with experimental results:

• The mass uptake absorption curve depends consistently on V_{ftow}: this is reasonable since the carbon fibres are hydrophobic and may impact significantly the full sorption curve,

• The numerical curve agrees with experimental curve for a tow fibre volume fraction value of around 70%: this is in good agreement with V_{ftow} measurements carried out on the microstructure by optical microscopy,

• Even for the optimal V_{ftow} value, the mass uptake behaviour is only approximately Fickian. Differently from what predicted by the Fick's law, slight deviations from linearity (wrt square root of time) are observed for short conditioning times. It must be remembered that the resin behaviour is taken as Fickian, therefore the behaviour observed in Fig. 10 is related to a structural effect related to the peculiar geometry of the ERP textile architecture. In fact, in this architecture, resin rich layers are situated close to the external surfaces directly exposed to the environment. Therefore, in the first phases of the absorption, water diffuses almost exclusively in superficial matrix rich layers at a speed which is close to the resin diffusivity values. When time advances, water reaches tow material and diffusivity slows down. This explains the almost bi-linear behaviour observed in Fig. 10, in which mass uptake takes place faster in the first phases of diffusion (higher slopes) then slows down afterwards (slower slopes after around 5 $h^{1/2}$).

Coherently with the physical interpretation of the phenomenon, the effect is more pronounced in numerical curves with higher V_{ftow} values. However, for optimal V_{ftow} values (70%) the deviation from Fickian behaviour is very low and-considering the experimental scatter-can be hardly appreciated experimentally.

Simulation results in Fig. 10 give confidence in the numerical model, which can be then employed for the understanding of the material diffusion behaviour and simulation of diffuso-mechanical performance of the ERP. This last issue is under study and will be the object of future communications.

4. Conclusions

The paper has presented a first step towards the understanding of the water diffusion behaviour of RTM textile materials for aircraft applications and focused on the development of experimental and numerical approaches to characterize the diffusion kinetics within the material.

Samples which are representative of the materials architecture have been manufactured and subjected to gravimetric tests. Analysis of results has been carried out with the aid of a diffusion model reconstructing the architecture of the samples helps identifying the diffusion behaviour of the material. The model is useful to reconstruct numerical charts of the full water concentration field which is not accessible experimentally. Moreover, numerical models can be employed for the understanding of the material diffusion behaviour and simulation of diffuso-mechanical performance of the ERP. This last issue is under study and will be the object of future communications.

Acknowledgments

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