WATER DIFFUSION IN COMPOSITE MATERIALS – INTERFACIAL PHENOMENA: EXPERIMENTAL, ANALYTICAL AND NUMERICAL APPROACH

Y. Joliff[1*], L. Belec[1], M.B. Heman[1], J.F. Chailan[1]

[1]*MAPIEM, EA 4323, Institut des Sciences de l'Ingénieur de Toulon et du Var, Avenue Georges Pompidou, BP56, 83162 La Valette-du-Var cedex, France*

**yoann.joliff@univ-tln.fr*

Keywords: Composites; Interphase; Water diffusion; Finite element analysis.

Abstract

This paper deals with the water diffusion in unidirectional composite by three approaches: experimental measurements, analytical and numerical models. In the initial state, microthermal analysis of matrix shows an increase of molecular mobility at decreasing distance from surface fibres defining an interphase around each monofilament. A Fickian diffusion kinetic was determined from water absorption measurements on both the resin and the UD composite. The numerical simulation shows that the matrix is strongly modified by the presence of fibres, compared to the resin alone. A matrix diffusion coefficient higher than the bulk resin one must be used to fit correctly the experimental data. This is consistent with the increase in molecular mobility highlighted by µTA measurements.

1 Introduction

The mechanical properties of thermosetting-based composites used for aeronautical parts are generally high at initial stage but drop under service conditions due to the mechanical and environmental stresses. Many physical and chemical effects with complex interactions may be involved in ageing process in humid environments. The drop in mechanical properties is often attributed to the degradation at matrix/reinforcement interface or interphase [1, 2, 3]. Recent techniques show an interphase stiffness lower than the matrix stiffness over several micrometers around each monofilament due to an incomplete curing [4-5] or to plasticizing effects from fibre treatment [6-7]. The interphase can then be characterized by a molecular mobility different from the bulk matrix one, which influences water diffusion and solubility inside the composite material [7].

Diffusion of water through epoxy resins has been widely studied [8-9]. The diffusion coefficients depend on many parameters as temperature, composition of resin and curing agent, fillers nature, etc.. Most resins follow a Fickian diffusion model [10-11], but Langmuir-type models also successfully describe water absorption of many epoxy systems [8-9]. The finite element approach of water diffusion phenomena in epoxy/glass fibre composites has often been performed using Fick model [12-13].

This study proposes to model the impact of interphase between fiber and matrix on water diffusion kinetics. The interphase properties are first characterized in term of molecular mobility. Then the diffusion kinetics of the unidirectional composite material and pure resin

material are determined. Finally, two modelling approaches (Fick and Numerical) are used to describe water diffusion. The confrontation of the results on ideal biphasic composite (numerical models) and real composite (experimental data) is correlated to the presence of interphases.

2 Materials and testing methods

The thermosetting matrix is a DGEBA-based epoxy resin (Araldite® LY556 from Ciba-Geigy) with aliphatic polyamine (XB3486 from Huntsman) selected as hardener at 33 parts by weight of resin. This resin has a long pot life compatible with the filament winding process at ambient temperature used to obtain laminas. E-glass fibres (300 Tex, 14 µm) have been treated with a commercial sizing. The unidirectional composites obtained are reinforced with 50%vol. glass fibres (Figure 1). Epoxy resin plates (without fibres) were also moulded following the curing cycles recommended by the manufacturer.

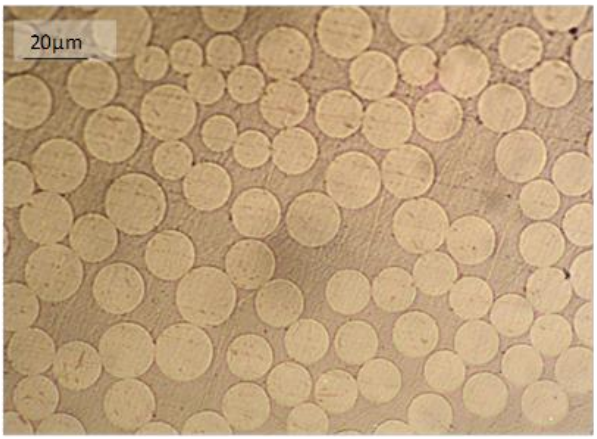

Figure 1. Unidirectional composite with 50%vol. glass fibres.

2.1 Micro-thermal Analysis

Micro-thermal analysis was used to characterize the composite microstructure and get information on the interphase size and properties. This technique combines the visualisation and positioning methods of atomic force microscopy (AFM) with the technology of thermal analysis with a calibrated thermoresistive probe [14]. A scan in apparent thermal conductivity of a few square micrometers can be obtained (Figure 2) and local thermal analysis can be performed during a heating ramp from ambient temperature to 250°C at 10°C/s. The aim is to follow the evolution of glass transition temperature at increasing distance from glass fibres The glass transition is indeed associated to a softening which gives a change in slope (dΔz/dT) corresponding to sensor vertical position during the ramp. A µTA 2990 from TA Instruments micro-thermal analyser was used. The thermal affected zone is estimated about 1µm diameter [15].

2.2 Hydrothermal ageing

Normalized composite and resin plates (75x75x2 mm^3) were immersed at 70°C in deionized water up to saturation (between 8 and 16 weeks) according to aerospace standard [16].The water uptake is measured regularly on a precision Ohaus balance (+/- 0.5 mg) during ageing and the water absorption is then reported as a function of time or square root of time.

$$M(t)(\%) = \frac{m(t) - m(0)}{m(0)}.100 \quad \textbf{(1)}$$

where m(0) et m(t) are sample mass at the initial state and at the time t.

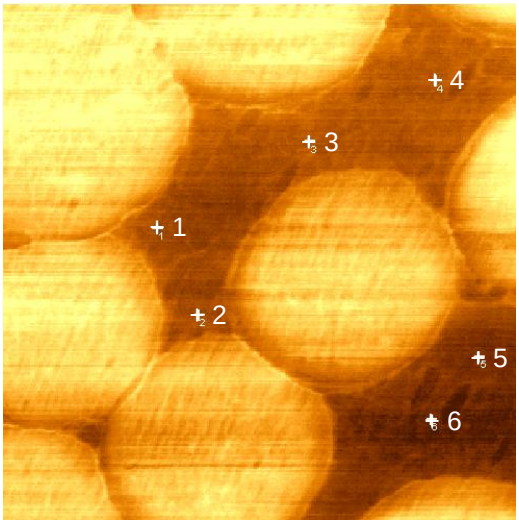

Figure 2. Apparent thermal conductivity image obtained on UD composite by scanning at 50°C and example of Localized Thermal Analysis measurements (1-6).

3 Analytical models: Fick model

In the literature several analytical models are proposed to describe the diffusion kinetic of epoxy-matrix composite systems. In first approximation, a fickien kinetic can be used:

$$\frac{M_t}{M_S} = 1 - \left[\frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}exp\left(\frac{D(2n+1)^2\pi^2 t}{4h^2}\right)\right] \quad \textbf{(2)}$$

where Mt is water mass absorbed at the time t, Ms is saturated water mass, D is diffusion coefficient and h is plate thickness.
At short time, this equation can be simplified to describe the linear part and to give the diffusion coefficient D:

$$\frac{M_t}{M_S} = \frac{2}{h}\sqrt{\frac{Dt}{\pi}} \quad \textbf{(3)}$$

Absorption curve (mass concentration vs square time) for epoxy resin obtained by experimental measurement has permitted to calculate the diffusion coefficient D. Indeed, D value can be directly calculated from the gradient a of the curve linear part:

$$a = \frac{\Delta M_\infty}{M_0}.\frac{4}{h}\sqrt{\frac{D}{\pi}} \quad \textbf{(4)}$$

The diffusion coefficient of the epoxy-resin is 15.10^{-13} $m^2.s^{-1}$. This value will also be used in finite element model for the composite matrix.

4 Finite element models

A 2D finite element model has been realized in the commercial software Abaqus™ to simulate the water diffusion along specimens [17-18]. Due to symmetries, only half thickness has been used for simulation. Water immersion has been modelled by a boundary condition (Figure 3).

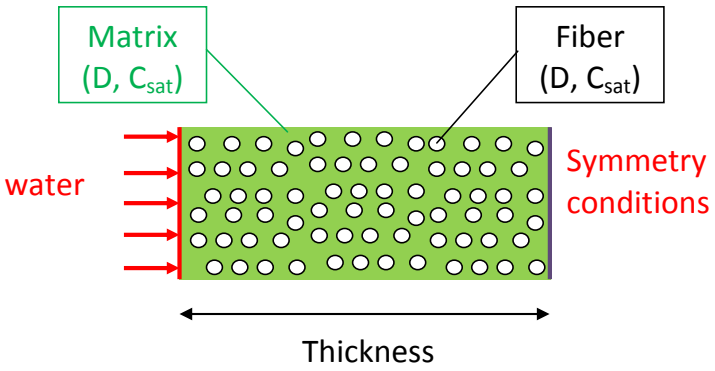

Figure 3. Modelling of water diffusion in UD composite.

	Matrix epoxy aliphatic	Glass fiber
D ($m^2.s^{-1}$)	15 e^{-13} *	1 e^{-30} **
Ms (%)	2.29 *	1 e^{-30} **

* Experimental value
** Arbitrary values (none water uptake in the range time considering)

Table 1. Properties materials used in numerical model.

5 Results and discussion

5.1 Local measurement results

Several authors [4-7] have shown than the introduction of glass fibre modified the matrix properties, which will influence the water uptake behaviour. An evolution of molecular mobility around glass fibres should lead to an evolution of glass transition temperature of the polymer network. The µTA enables to follow the softening temperature Ts vs distance from monofilament (Figure 4).

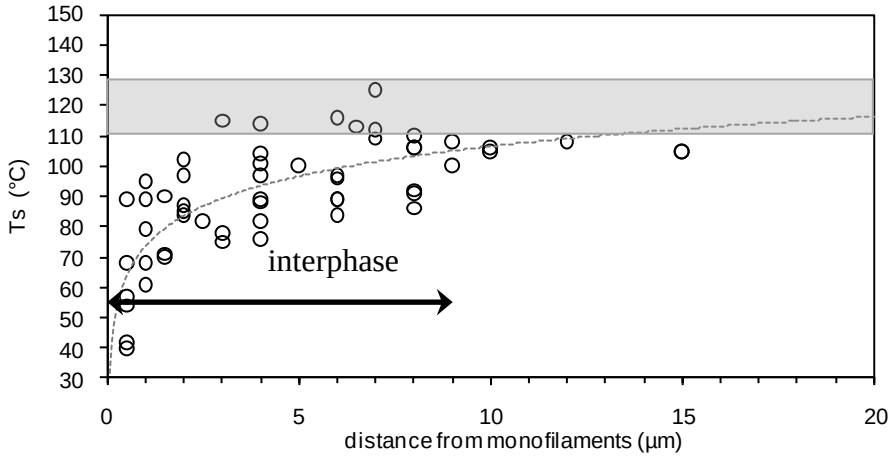

Figure 4. Ts evolution vs distance from monofilament for epoxy/glass fibre composite with bulk resin Ts measurements in grey area as reference.

The results show a decrease of the softening temperature when the distance from fibres surface decreases. Different Ts measurements on bulk resin have also been performed and superimposed for comparison in a grey area. The interphase region is then defined by the area where the softening temperature is lower than the softening temperature of the bulk. In that case the interphase is nearly 10 µm width and the softening temperature is highly decreased compared to the resin one. This phenomenon is attributed to incomplete curing [4-5] or plasticizing effects from fibre treatment [6-7]. The dispersion of results is explained by heterogeneities of cross-link density and by heterogeneous sizing distribution on fibres.
These results confirm that the resin properties are strongly modified by fibres introduction. Moreover, a plasticized or under crosslinked network will probably change the diffusion kinetics compared to the one of bulk resin network. The modelling of composite and resin water uptake should confirm these assumptions.

5.2. Resin diffusion kinetics

The results of analytical and numerical models have been compared to experimental values. The models are in good agreement with the matrix diffusion kinetics (Figure 5). Then, the diffusion coefficient value of $15.e^{-13}$ $m^2.s^{-1}$ will be used to describe the matrix composite behaviour.

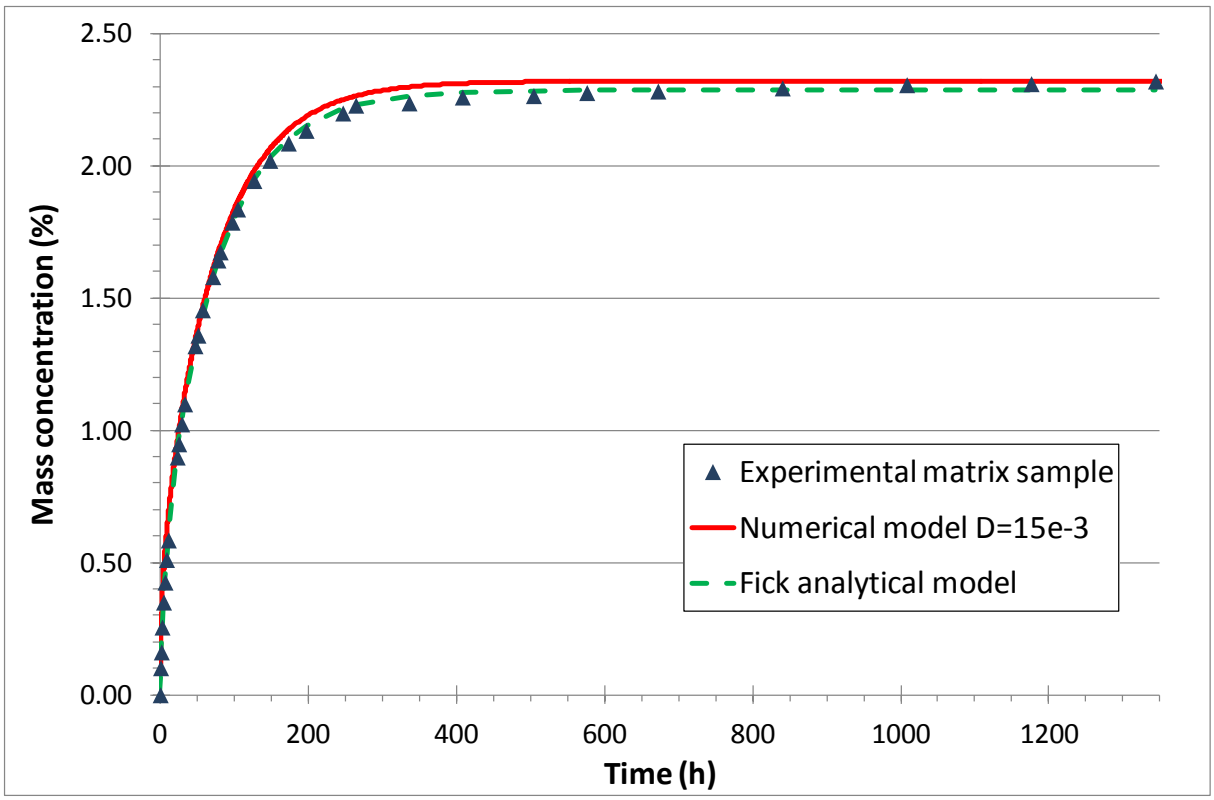

Figure 5. Resin absorption curve obtained by experimental measurement, analytical (Fick) and finite element calculus for epoxy resin material.

5.3. Composite diffusion kinetics

A previous study about the impact of glass fibre arrangement has been shown that it has a significant impact on mass diffusion results [19]. Analytical (Fick) and numerical models have then been compared to experimental values (Figure 6). At short times, numerical results remain lower than experimental and analytical values which confirm that the diffusion coefficient of the matrix is much higher than the resin one.

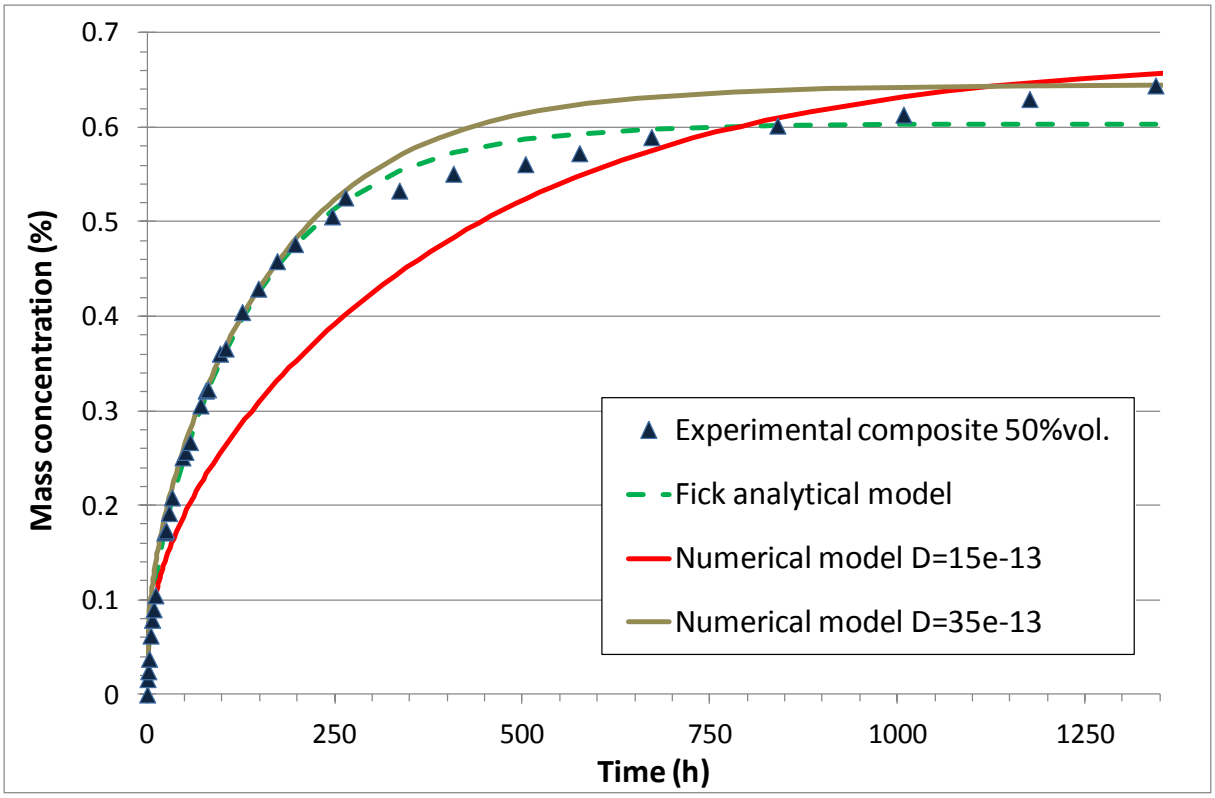

Figure 6. Matrix absorption curve obtained by experimental measurement, analytical (Fick) and numerical calculus for composite samples (50% volume).

To fit experiment results with numerical model, the matrix diffusion coefficient has then been increased up to D_{matrix} = 35 e^{-13} $m^2.s^{-1}$. The gap between resin and matrix values suggests that the matrix has been highly modified by fibre introduction as previously shown by local thermal measurements.
Moreover, the models developed in this work are based on simplified microstructure which underestimates closed volumes. It was shown that these closed volumes areas decreased the saturation level. In addition, the number of fibres in contact influences barrier effects and consequently, the diffusion rate. A more realistic geometrical interpolation should then improve the saturation behaviour and the diffusion kinetics modelling.

6 Conclusions

An interphase of several micrometers width with a higher molecular mobility than the bulk resin is present around each monofilament from gravimetric measurements in immersion, the water uptake behavior was considered as Fickian in first approximation for both the composite and the resin. Kinetics diffusion parameters were then used in numerical models.
Despite a simplified microstructure description, taking into account barrier effect (contact fibers) and proportion of closed matrix areas, numerical results are close to experimental and analytical values.
The numerical simulation shows that the matrix is strongly modified by the presence of fibres, compared to the resin alone. Indeed, a matrix diffusion coefficient higher than the bulk resin one must be used to fit correctly the experimental data. This is consistent with the increase in molecular mobility highlighted by µTA measurements.

References

[1] Chateauminois A., Vincent L., Chabert B., Soulier J.P. Study of the interfacial degradation of a glass-epoxy composite during hygrothermal ageing using water diffusion measurements and dynamic mechanical thermal analysis. *Polymer,* **35**, pp. 4766-4774 (1994).
[2] Griswold C., Cross V.M., Kjerengtroen L., Kellar J.J. Interphase variation in silane-treated glass-fibre-reinforced epoxy composites. *J. Adhesion Sci. and Tech.*, **19**, pp. 279-290 (2005).
[3] Olmos D., Gonzales-Benito J. Composites formed by glass fibers and PS-Modified epoxy matrix. Influence of the glass fibers surface on the morphology and mechanical properties of the interphases generated. *Polymer Composites*, **31**, pp. 946-955 (2010).
[4] Tillman M.S., Hayes B.S., Seferis J.C. Examination of interphase thermal property variance in glass fibre composites. *Thermochimica Acta*, **392-393**, pp. 299-302 (2002).
[5] Johnson F.J., Cross W.M., Boyles D.A., Kellar J.J. Complete system monitoring of polymer matrix composites. *Composites Part A,* **31**, pp. 959-968 (2000).
[6] Bartolomeo P., Chailan J.F., Vernet J.L. Dielectric investigation of interphase formation in composite materials. II. Relaxation process. *J. Polymer Sci. Part B,* **38**, pp. 2162-2169(2000).
[7] Mallarino S., Chailan J.F., Vernet J.L. Interphase investigation in glass fibre composites by micro-thermal analysis. *Composites Part A*, **36**, pp. 1300-1306 (2005).
[8] Carter H.G., Kibler K.G. Langmuir-Type Model for Anomalous Moisture. Diffusion in Composite Resins. *J. Composite Materials,* **12**, pp. 118–131 (1978).
[9] Popineau S., Rondeau-Mouro C., Sulpice-Gaillet C., Shanahan M.E.R. Free/bound water absorption in an epoxy adhesive. *Polymer*, **46**, pp. 10733–10740 (2005).
[10] Luo S., leisen J., Wong C.P. Study on mobility of water and polymer chain in epoxy and its influence on adhesion. *J. Applied Polymer Sci.*, **85**, pp. 1–8 (2002).
[11] De Nève B., Shanahan M.E.R. Water absorption by an epoxy resin and its effect on the mechanical properties and infra-red spectra. *Polymer*, **34**, pp. 5099–5105 (1993).
[12]Boukhoulda B.F., Adda-Bedia E., Madani K. The effect of fiber orientation angle in composite materials on moisture absorption and material degradation after hygrothermal ageing. *Composite Structures*, **74**, pp. 406–418 (2006).
[13] Vaddadi P., Nakamura T., Singh R.P. Transient hygrothermal stresses in fiber reinforced composites: a heterogeneous characterization approach. *Composites: Part A,* **34**, pp. 719–730 (2003).
[14] Haessler R., Muhlen E. An introduction of micro-TA and its application to the study of interfaces. *Thermochemica Acta*, **361**, pp. 113-120 (2000).
[15] Joliff Y., Belec L., Chailan J. F. Finite element analysis of the material's area affected during a micro thermal analysis applied to homogeneous materials. *J. Surface Engineered Materials and Advanced Tech.*, **1**, pp. 1-8 (2011).
[16] AFNOR NF EN 2489: Aerospace series. Fibre reinforced plastics. Determination of the action of test fluids.
[17] ABAQUS v.6.10-2, Abaqus Analysis User's Manual - 6.8 Mass diffusion analysis, Dassault System Simulia Corp., Providence, RI, USA, 2010.
[18] Crank J. *The Mathematics of Diffusion*. Clarendon Press, Oxford (1956).
[19] Joliff Y., Belec L., Heman M.B., Chailan J.F. Experimental, analytical and numerical study of water diffusion in unidirectional composite materials – Interphase impact. *Computational Materials Science Special Issue: IWCMM -21*, in press.