IDENTIFICATION OF 3D MOISTURE DIFFUSION COEFFICIENTS FOR CARBON/EPOXY LAMINATES

J.Jedidi[1], F.Jacquemin[2], A.Vautrin[1]

[1] Mechanical and Materials Engineering Department, Ecole des Mines de Saint-Etienne
158 Cours Fauriel, 42023 Saint-Étienne France
[2] Institut de Recherche en Génie Civil et Mécanique, Université de Nantes
Boulevard de l'Université, BP406, 44602 Saint-Nazaire

ABSTRACT

An identification method is proposed to extract the diffusion properties from the gravimetric curves of a composite material used in Super Sonic Transportation. It consists in identifying the maximum moisture content and the diffusivity coefficients at the same time, in contrast with the usual procedure which identify these parameters separately by calculating the slope and the plateau value. The solution consists in seeking the unknowns of the problem by minimizing the standard deviation between the experimental gravimetric curve and the analytical solution according to Fick's models. The results apply during moisture absorption when the relative humidity and the temperature of the environment are constant. Test procedures are described for determining experimentally the values of the maximum moisture content and the diffusivity coefficients of this composite material. A series of tests using unidirectional, quasi-isotropic and cross-ply Carbon IM7 Epoxy 977-2 composites were performed in a specific environment: at 80°C and moist air at 80% HR. The test data support the analytical results and provide the moisture diffusion properties of each stacking sequence laminate thanks to the identification method.

1- INTRODUCTION

Moisture and temperature affect strongly the performance of polymer matrix composites and cause dimensional changes due to moisture uptake and thermal expansion. These parameters can have a critical effect on long-term structural durability. Therefore, composite material response to moist environment must be characterized [1,2].

The study is related to a Super Sonic Transportation application where polymer matrix composites utilized in primary structures are subjected to particular hygrothermal flight-cycles. The original material of interest constitutes a wing element made of a Carbon/Epoxy IM7/977-2 quasi-isotopic 30 plies laminate, which can be assimilated to an infinite plate whose thickness is 4 mm. The particular point that should be investigated in that case is the effect on the long-term of the high service temperature, around 130°C, during the supersonic flight resulting in the heating of the structural elements during the flight [3]. These particular conditions of supersonic flight will induce on the long-term a material drying, which constitute an entirely new situation for these materials, contrasting with a classical subsonic flight at low temperature. However, in order to prove the material drying during the supersonic flight-cycles, the moisture concentration profile through the thickness of the structure must be calculated at each cycle. It requires the knowledge of the moisture diffusion coefficients.

Thus, the objective of this investigation is to identify moisture diffusion coefficients and maximum moisture content from gravimetric curves of Carbon/Epoxy IM7/977-2 laminates. The identification methodology is based on Fick's law.

2- IDENTIFICATION METHOD

2.1- One-dimensional Fickian diffusion:

Moisture diffusion process through composite materials is frequently modelled by the one-dimensional Fick's law written as follows for an infinitely large plate [4]:

$$\frac{\partial c}{\partial t} = D_3 \frac{\partial^2 c}{\partial z^2} \quad for\ 0 \le z \le e\ and\ t > 0 \tag{1}$$

where c is moisture concentration, D_3 is the diffusion coefficient in the thickness direction, e is the plate thickness and z is the position in the thickness direction.

Initial and boundary conditions for an infinite plate are:

$$c = c_i \quad for\ 0 \le z \le e\ and\ t < 0 \tag{2}$$

$$c = c_\infty \quad for\ z < 0;\ z > e\ and\ t \ge 0$$

where c_i and c_∞ are respectively the initial and saturated moisture concentrations.

The solution of the one-dimensional Fick's problem can be expressed as [4]:

$$\frac{c_t - c_i}{c_\infty - c_i} = 1 - \frac{\pi}{4}\sum_{i=0}^{\infty}\frac{1}{(2i+1)^2}\sin\left(\frac{(2i+1)\pi z}{e}\right)\exp\left(-\frac{(2i+1)^2\pi^2 D_3 t}{e^2}\right) \tag{3}$$

If we integrate equation (3) with respect to the space variable, we are able to determine the total masse of moisture absorbed by the plate at any time t. The solution of the one-dimensional Fick's problem is now described by equation (4) which determines the percentage of moisture in the plate as a function of time, with constant temperature and relative humidity [1,4]:

$$M_t = M_\infty\left(1 - \frac{8}{\pi^2}\sum_{i=0}^{\infty}\frac{1}{(2i+1)^2}\exp\left(-\frac{(2i+1)^2\pi^2 D_3 t}{e^2}\right)\right) \tag{4}$$

where M_t and M_∞ are respectively the total mass of moisture in the plate at time t and at saturation divided by the masse of dry specimen.

The one-dimensional Fick's diffusion is characterised by M_∞ the maximum moisture content, asymptotically reached after a long period of exposure at constant temperature and moisture and D_3 the coefficient of diffusion which governs the speed of moisture diffusion through the material in the thickness direction.

The usual identification method [1,5] consists in extracting the maximum moisture content M_∞ from the gravimetric curve, which is the plateau value. Then, the diffusion coefficient D_3 is calculated from the linear part of the gravimetric curve at early stages. D_3 is obtained from the initial slope of the gravimetric curve as a function of the square root of time using two points at times t_1 and t_2 [1,5]:

$$D_3 = \pi\left(\frac{e}{4M_\infty}\right)^2\left(\frac{M_2 - M_1}{\sqrt{t_2} - \sqrt{t_1}}\right)^2 \tag{5}$$

We propose now to identify at the same time the set of parameters (M_∞, D_3). The identification is based on confronting the analytical solution on the one-dimensional Fick's problem (4) with the experimental statement of the mass variation for each specimen [6]. Particularly, we minimize the standard deviation between the analytical solution (4) and the experimental moisture uptake (fig.2, 3 and 4) to identify the set of parameters (M_∞, D_3): the solution consists in seeking the unknowns of the problem by the method of least squares. Identification method is used for three specimens at the same time. Experimental uptake curve is compared to that resulting from identified results afterwards.

2.2- Three-dimensional Fickian diffusion:

In the case of a thick plate of finite dimensions, the diffusion process through the edges can not be neglected. The 3-D Fick's law is written as:

$$\frac{\partial c}{\partial t} = D_1 \frac{\partial^2 c}{\partial x^2} + D_2 \frac{\partial^2 c}{\partial y^2} + D_3 \frac{\partial^2 c}{\partial z^2} \tag{6}$$

where D_1, D_2 and D_3 are the 3D diffusion coefficients governing the speed of moisture absorption through the material in every direction.

Initial and boundary conditions are:

$$c = c_i \; for \begin{cases} -\frac{L}{2} \le x \le \frac{L}{2} \\ -\frac{l}{2} \le y \le \frac{l}{2} \\ -\frac{e}{2} \le z \le \frac{e}{2} \end{cases} at\ t = 0 \quad and \quad c = c_\infty for \begin{cases} x \le -\frac{L}{2}; x \ge \frac{L}{2} \\ y \le -\frac{l}{2}; y \ge \frac{l}{2} \\ z \le -\frac{e}{2}; z \ge \frac{e}{2} \end{cases} at\ t \ge 0 \tag{7}$$

The solution of the 3-D Fick's problem can be expressed as [1,4]:

$$\begin{aligned} \frac{c_t - c_i}{c_\infty - c_i} = 1 - \frac{64}{\pi^3} \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} \sum_{k=0}^{\infty} \frac{(-1)^i (-1)^j (-1)^k}{(2i+1)(2j+1)(2k+1)} \cos\frac{(2i+1)\pi x}{L} \cos\frac{(2j+1)\pi y}{l} \cos\frac{(2k+1)\pi z}{e} \\ \times \exp\left(-\pi^2 t \left(D_1 \left(\frac{2i+1}{L}\right)^2 + D_2 \left(\frac{2j+1}{l}\right)^2 + D_3 \left(\frac{2k+1}{e}\right)^2 \right) \right) \end{aligned} \tag{8}$$

If we integrate equation (8) with respect to the space variables, we obtain:

$$\frac{M_t}{M_\infty} = \left[1 - \left(\frac{8}{\pi^2}\right)^3 \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} \sum_{k=0}^{\infty} \frac{1}{\left((2i+1)(2j+1)(2k+1)\right)^2} \exp\left(-\pi^2 t \left(D_1 \left(\frac{2i+1}{L}\right)^2 + D_2 \left(\frac{2j+1}{l}\right)^2 + D_3 \left(\frac{2k+1}{e}\right)^2 \right) \right) \right] \tag{9}$$

We will now identify at the same time the four unknowns (M_∞, D_1, D_2, D_3). The identification is based on seeking the four unknowns of the problem by minimizing the standard deviation between the analytical solution (9) and the gravimetric curve (fig.2, 3 and 4) using a Gauss-Newton algorithm [6]. Identification method is used for three specimens at the same time. Experimental uptake curve is compared to that resulting from 1D and 3D identified results.

Extensive numerical simulations were carried out on various specimen geometries with numerical values of (M_∞, D_1, D_2, D_3) given by EADS-CCR in order to optimise and validate the identification method. According to these simulations, three types of specimens were selected

(Fig.1). Unidirectional 0° are used to identify $D_{//}$ and $D_{\perp}$, which stand for diffusion coefficients parallel and perpendicular to the fibres direction respectively. Quasi-isotropic and $[\pm 45]_{4S}$ specimens are used to identify D_{tr} and D_{eq}, which stand for diffusion coefficients through the thickness and parallel to the plies respectively (Fig.1).

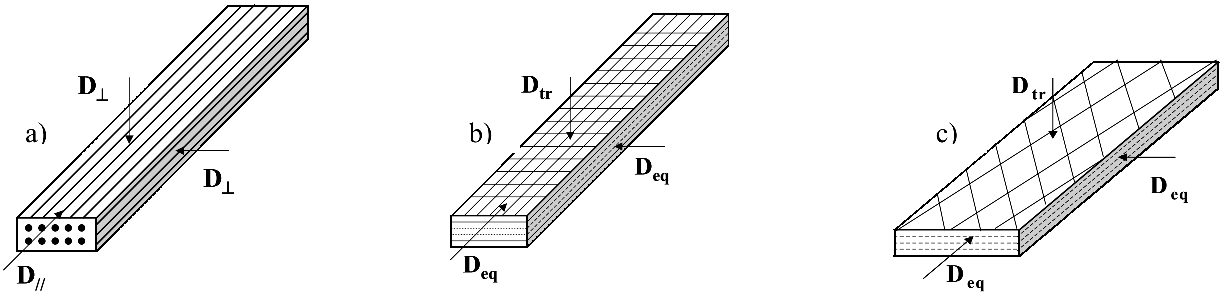

Fig.1: Different type of testing specimens used for identification.
a) Unidirectional 0 specimen 200x10x2mm, b) Quasi-isotropic specimen 200x10x2mm,
c) $[\pm 45]_{4S}$ specimen 110x25x2mm.

The problem has been simplified and only three unknowns will be identified:

- (M_{∞}, $D_{//}$, $D_{\perp}$) for the unidirectional specimens,
- (M_{∞}, D_{eq}, D_{tr}) for the quasi-isotropic and $[\pm 45]_{4S}$ specimens.

3- RESULTS & DISCUSSION

In order to predict the moisture content of the IM7/977-2 laminates, the maximum moisture content M_{∞} and the diffusivity coefficients must be known (9). Moisture uptake tests were performed in order to determine these parameters and verify whether the diffusion process through IM7/977-2 laminates is well described by Fick's law. The complete test procedure is detailed below:

- Test specimens: Three test specimens are cut in each IM7/977-2 thin plate laminates of different stacking sequences: unidirectional, quasi-isotropic and cross-ply $[\pm 45°]_{4S}$. The thickness of these plates is 2 mm. Thus, specimens thickness is twice smaller than the original 4 mm thickness plate in order to reduce the conditioning time which is proportional to the square of the plate thickness [1,4]. Specimen geometry is previously chosen to minimize the diffusion through the edges.

- Specimen drying: Specimens are completely dried in a vacuum oven during 3 weeks at 130°C. We decide to fix the drying temperature at 130°C simply because it is the in-service flight temperature [3]. We could have a higher drying by imposing a temperature over 130°C, but such a high temperature has no particular meaning regarding the in-service conditions and it could activate some degradation phenomena such as thermo-oxidation which do not exist for the material under flight-cycles. Finally, the dry weight is measured for each specimen.

- Moisture uptake tests: Specimens are placed in a constant temperature and constant moisture environment (80°C and 80% HR) and their weights are recorded as a function of time. This special environment is chosen in order to accelerate the moisture uptake process. Indeed, according to equation (10), the more the temperature is high, the more the moisture diffusion kinetic is fast [1]. Moreover, according to equation (11), the maximum moisture content grows with the relative humidity [1]:

$$D = D_0 \exp\left(-\frac{E_a}{RT} \right) \tag{10}$$

$$c_\infty = a\ \Phi^b \tag{11}$$

where D_0 is a constant in mm^2/s, E_a is an activation energy in kcal/mol, R is the constant of perfect gases, T is the material absolute temperature, Φ is the ambient relative humidity, a and b are constants depending only on the material.

Finally, moisture uptake test duration was about 10 weeks. The moisture content is plotted as a function of the square root of time for each specimen (fig.2, 3 and 4).

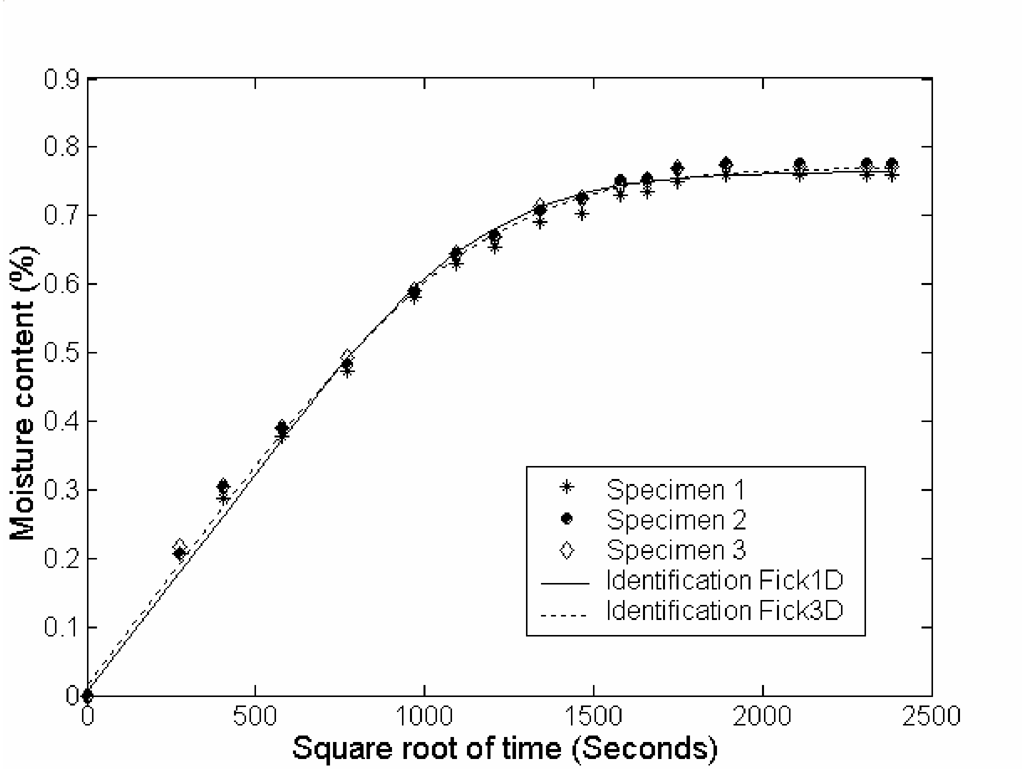

Fig.2: Experimental curves of moisture uptake as a function of square root of time and associated identifications for 3 unidirectional 0 specimens.

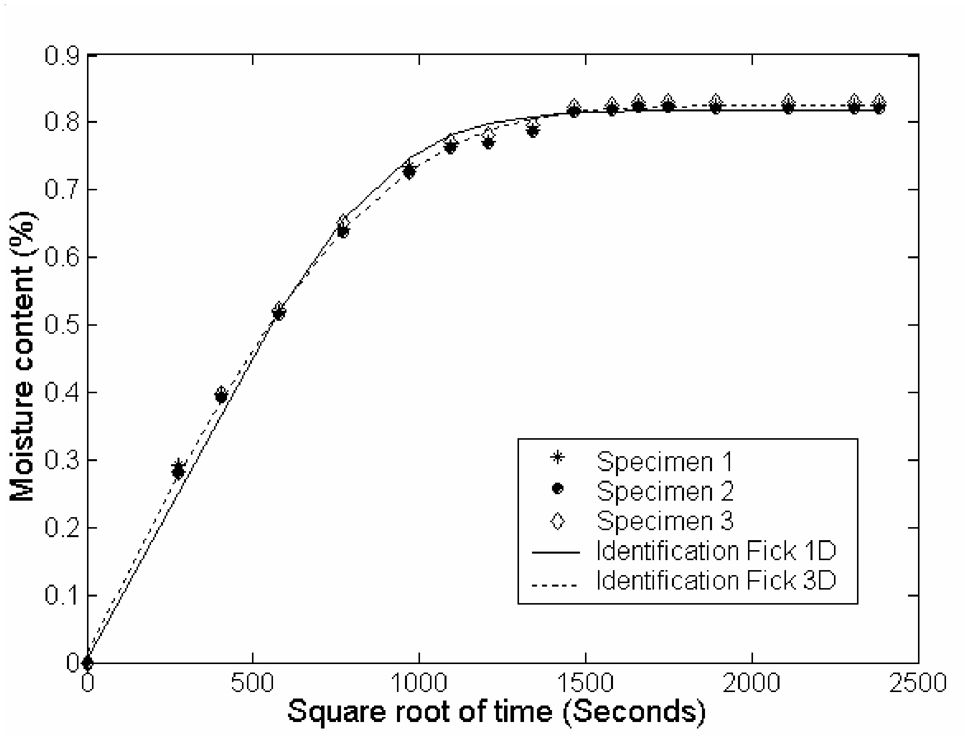

Fig.3: Experimental curves of moisture uptake as a function of square root of time and associated identifications for 3 quasi-isotropic specimens.

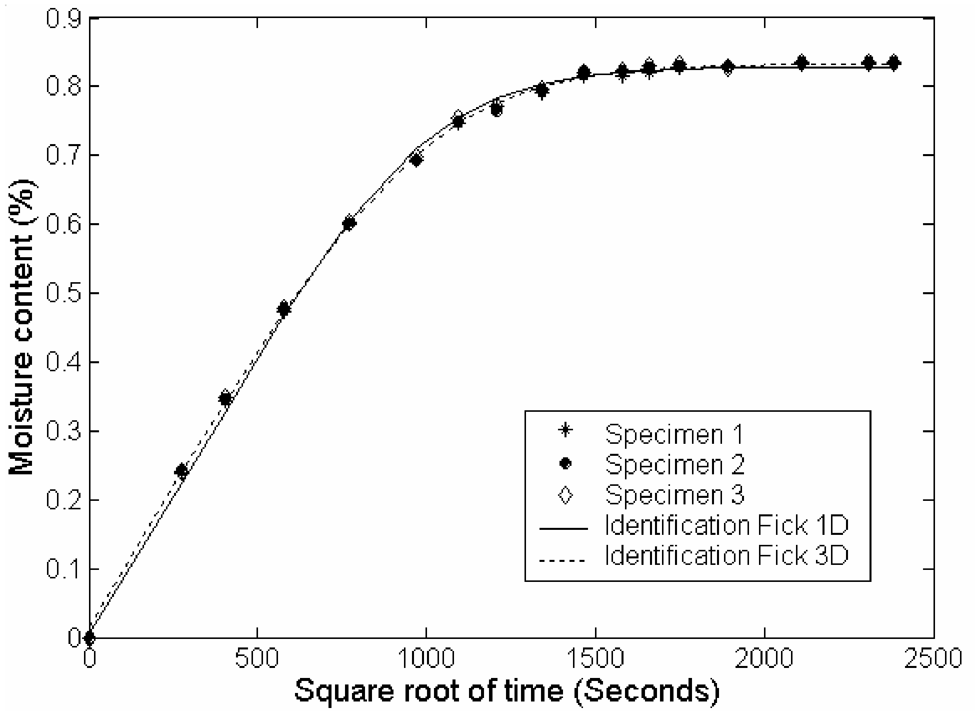

Fig.4: Experimental curves of moisture uptake as a function of square root of time and associated identifications for 3 $[\pm 45]_{4S}$ specimens.

The moisture contents are shown as a function of square root of time for each stacking sequence (fig.2, 3 and 4). Experimental results confirm the Fickian properties of the material beforehand assumed for identification.

Model	Diffusion parameters	UD 0	QI	$[\pm 45]_{4S}$
1D Fick's law	$\mathbf{M_\infty}$ (%)	0,76	0,82	0,83
	D (mm²/s)	$D_\perp = 5{,}6\ 10^{-7}$	$D_{tr} = 9{,}6\ 10^{-7}$	$D_{tr} = 7{,}5\ 10^{-7}$
3D Fick's law	$\mathbf{M_\infty}$ (%)	0,77	0,82	0,83
	D (mm²/s)	$D_{//} = 3{,}80\ 10^{-6}$ $D_\perp = 4{,}6\ 10^{-7}$	$D_{eq} = 3{,}98\ 10^{-6}$ $D_{tr} = 5{,}8\ 10^{-7}$	$D_{eq} = 4{,}01\ 10^{-6}$ $D_{tr} = 6{,}0\ 10^{-7}$

Table 1: Diffusion parameters identified according to the 1D and 3D Fick's models for each stacking sequence specimens.

Lest us focus on the 3-D diffusion coefficients of unidirectional specimens (Table.1). The diffusion coefficient along the fibres direction $D_{//}$ is ten times larger than the through thickness diffusion coefficient which is comforted by other results found by Blikstad [5]. This phenomenon can be explained by the theory of the crossed path by water molecules during diffusion process, where the fibres embedded in the matrix are assumed to act as a barrier to the penetrating water molecules [7]. If water molecules diffuse perpendicularly to the fibres direction, they will go round the fibres and moisture diffusion takes complicated and longer path in comparison with the rectilinear path where water molecules diffuse along the fibres direction. Thus, $D_{//}$ is greater than $D_\perp$. In fact, the diffusion process along the fibres direction is faster since the effective distance crossed by water molecules is smaller than the one crossed perpendicularly to the fibres.
Table 1 shows the large increase of the diffusion coefficient along the fibre direction ($D_{//}$ for UD) and the influence of the internal state of stress on the diffusion parameters resulting in higher equilibrium water concentrations and coefficients of diffusion for QI and $[\pm 45°]_{4S}$ than for UD because of tensile residual stresses. Moreover, the values for those latter laminates remain very close one from an other due to the same state of internal stress.
Besides, according to these figures we notice that the stacking sequence has an effect on the diffusion properties. In fact, we notice that unidirectional specimens tend to absorb less moisture than the cross-plies during the same period of time. The change of the moisture concentration with time is linked to the stacking sequence and specimen geometry. Let us only focus on the difference between UD and QI, since the fibre volume fraction is constant that difference is mainly due to the stacking sequence. For UD laminates, the manufacturing residual stresses are equal to zero at the mesoscopic level, however in the case of QI or cross-ply $[\pm 45]_{4S}$ laminates the plies sustain a transverse tension at temperature below the manufacturing temperature. Therefore, we can understand that moisture concentration could be higher for QI laminates. This qualitative approach should be strengthened by a refined analysis in the future.

4- CONCLUSION

In the present paper an original method is proposed to identify the diffusion properties from the gravimetric curves of IM7/977-2 laminates according to Fickian models. It consists in identifying

the maximum moisture content and the diffusivity coefficients at the same time, in contrast with the usual procedure which identify these parameters separately by calculating the slope of the gravimetric curve at early stages and the plateau value at saturation. A series of tests using unidirectional, quasi-isotropic and cross-ply $[\pm 45]_{4S}$ laminates were performed at 80°C and moist air at 80%. The test data support the analytical results and provide the moisture diffusion properties of each stacking sequence laminate thanks to the identification method.
According to the 1D identified parameters, we notice that the stacking sequence has an effect on the diffusion properties. In fact, unidirectional specimens tend to absorb less moisture than the quasi-isotropic and the cross-ply specimens during the same period of time since the slope and the plateau value are smaller. This phenomenon is probably related to the internal state of stress. Moreover, according to the 3D identified parameters for unidirectional specimens, we found that the diffusion coefficient along the fibre direction $D_{//}$ is ten times larger than the through thickness diffusion coefficient $D_{\perp}$. This result can be explained by calculating the crossed path by water molecules during diffusion process.
Moisture diffusion properties of the IM7/977-2 laminates have been carefully characterised, it is now possible to calculate the moisture concentration profile through the thickness of the wing structure after each supersonic flight-cycle and study the hygrothermal behaviour of the material under service conditions [8,9].

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