Experimental/numerical study of anisotropic water diffusion in glass/epoxy composites

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Abstract. In this work a glass/epoxy composite commonly used in wind turbine blades is exposed to a humid environment at an elevated temperature. To research the anisotropic diffusion behaviour observed in unidirectional composite specimens, experimental results of slices cut along the three directional planes of the laminate immersed in demineralised water at 50°C are coupled with numerical modelling. The weight of the slices was measured at regular intervals, from which the uptake behaviour could be deduced. The process was modelled using a 3-dimensional RVE of the material, where diffusion is modelled as steady-state and the diffusivity in each direction was measured by applying concentration gradients to the model. The experimental data shows similar water uptake behaviour for samples in both transverse directions, while the water uptake in the fibre direction was significantly faster. A proper fit according to Fick’s law was obtained for the transverse direction, while this was not possible for the samples in fibre direction, suggesting a strong dependency of the diffusion behaviour on the fibre orientation. Results from the proposed numerical models show that the geometric effect of fibres acting as barriers for the water movement is indeed responsible for part of the observed anisotropy.

1. Introduction
Research on composite material usage optimization for wind turbine blades has been on the rise in the past few years, and particular focus is being given to reducing design uncertainty through a better understanding of material interaction with extreme service environments. Among many types of environmental attack, the combined influence of temperature and moisture ingression is often regarded as the most critical one [1]. Upon exposure to humid environments, composite structures tend to absorb water molecules through a diffusion process driven by pressure gradients. Experimental observations in glass/epoxy composites suggest that these water molecules are only capable of moving through and settling in the resin but not in the fibres [2]. This brings complexity to the diffusion phenomenon, since the water molecules have to go around the fibres for diffusion in the transverse direction [3], making the diffusion anisotropic. Furthermore, chemical interaction between the epoxy and fibre sizing creates an interphase region around the fibres where water diffusivity can be different from the one in bulk resin regions [4], which also promotes an anisotropic diffusion behaviour. In this work, an attempt is made to elucidate the anisotropic diffusion process using a combination of experimental measurements.
and microscopic numerical analysis.

In order to quantify the effect of fibre orientation on the diffusivity of water inside the material, it is important to measure the water uptake for isolated directions. To do so, a thick glass/epoxy composite panel was manufactured, from which equal sized specimens were made in the three directional planes of the laminate. The panel was made using a resin system commonly used in wind turbine manufacturing. After cutting, the samples were polished to avoid erroneous measurements due to rough damaged surfaces. Before starting the immersion, the specimens were dried at 50°C until a stable moisture-free state was achieved. The samples were subsequently immersed in demineralized water at 50°C and weighed at intervals. The resulting water uptake curves were then used in order to investigate the anisotropic nature of the diffusion process.

In order to investigate the cause of the anisotropy, the diffusion process was simulated on the microscale. A 3-dimensional Representative Volume Element (RVE) of the material was used and the diffusivity in each direction was computed by imposing periodic concentration boundary conditions and subjecting the RVE to a unit flux. In order to account for phenomena such as diffusion at the interphase, a level set field with constant radius was built around each fibre of the RVE and the diffusivity at each material point could be computed as a function of its distance to the nearest fibre. By fitting the experimental data using the numerical models, the relative contribution of each diffusion mechanism is assessed.

2. Experiments

2.1. Materials

The resin system is the Momentive EPIKOTE RIMR 135 / EPIKURE RIMH 1366, consisting of a monomer (70-100% 4,4-Isopropylidenediphenol-Epichlorohydrin Copolymer and 0-30% 1,6-Hexanediol Diglycidyl Ether) and a hardener (25-50% Alkyletheramine, 20-25% Isophoronediamine and up to 20% Aminoethylpiperazine) [5], mixed in a 100:30 ratio between monomer and hardener. For the UD laminate, the Saertex PPG 2002 2400tex (963 g/m²) unidirectional fabric was used, featuring a silanic coupling agent in order to improve interface adhesion.

A thick composite panel with 50 plies (approximately 30mm) was manufactured through vacuum infusion moulding. The panel was cured for 3 hours at 30°C and 5 hours at 50°C, and subsequently post-cured for 10 hours at 70°C. Fibres were oriented in a single direction (0°) for 95% of the total areal weight of the fabric, with 90° stabilization roving (sr) being used, accounting for 5% of the total areal weight. Since a pure UD panel was required to enable a direct link with the numerical results, the stability roving of the fabric was removed from each ply, except for a boundary region of about 5 cm at the top and bottom side. The fabric is stacked with the side of the stability roving being alternated, resulting in a balanced and symmetric laminate [(sr / 0°) – (0° / sr)]_{25}.

Specimens of about 30 x 30mm were cut from the panels using a water cooled diamond saw. After cutting slices in the three directional planes of the laminate, they were polished using a polishing machine with grid size up to 1200 in order to avoid erroneous measurements due to rough damaged surfaces. The slices were polished until a thickness of approximately 0.8 to 0.9 mm was reached. This uniform thickness was chosen to conform a width-to-thickness ratio of at least 30, and to minimise possible edge effects.

2.2. Conditioning

After polishing the slices, they were first dried in an exsiccator at 50°C in order to remove moisture content accumulated during manufacturing and storage. The samples were dried until a stable moisture-free state was achieved, while vacuum was applied to the exsiccator in order to accelerate the drying process and avoid the occurrence of oxidative reactions. Subsequently the
samples were weighed, measured and photographed, which was considered as reference state, followed by immersion in demineralised water at 50°C. At intervals, the samples were taken out of the water and weighed. The interval at which the samples were weighed decreased from hourly at the first day to twice on the second day and from there on, daily to every other day. Only one sample was taken out of the water at once, quickly wiped dry, weighed on an analytical balance and returned into the bucket of water, all within a timespan of about one minute to minimize the influence on the diffusion process.

![Diagram](image)

(a) Directions of diffusivity

Figure 1. Experimental results for water uptake and diffusivity in x, y & z-direction.

### 2.3. Results and Discussion

Specimens were cut in the three directional planes of the laminate (Figure 1(a)), where the x direction is the transverse plane in the through-thickness direction of the laminate, the y direction is the transverse plane in the in-plane direction of the laminate and the z direction is the fibre direction of the laminate. In Figure 1, for each direction a representative water uptake curve is shown, together with a fitted diffusivity curve according to Fick’s law. Because of the high width-to-thickness ratio of the samples, we can neglect the water diffusion through the edges and assume the diffusivity to be one-dimensional. The red dots represent the individual weight measurements performed at intervals, while the red line is a fit for the diffusivity described by the following equation [6]:

\[
D = \pi \left( \frac{h}{4w_\infty} \right)^2 \left( \frac{w_2 - w_1}{\sqrt{t_2} - \sqrt{t_1}} \right)^2
\]  

(1)
where $D$ is the diffusivity parameter, $h$ being the specimen thickness, $w_\infty$ the water uptake at saturation and $w_1$ and $w_2$ are two different uptake levels chosen from experimental measurements at the corresponding time values $t_1$ and $t_2$. The best fit is found by performing a least squares procedure on each possible combination of $w_1$ and $w_2$.

In Figure 1(b) and 1(c) with respectively the $x$ and $y$-direction, a similar uptake behaviour was found, which could be explained by a similar arrangement of the fibres inside the sample. For both directions the fibres are oriented in the plane of the sample, with the only difference being the through-thickness versus in-plane orientation of the sample plane. For these directions a close fit is obtained with the experimental data, suggesting that the assumption of Fickian uptake behaviour is valid. The $z$-direction (Figure 1(d)) on the other hand shows different uptake behaviour, where the sample reaches saturation in a shorter period of time. The initial part of the experimental data for this direction shows a poor fit with the Fickian diffusivity curve, suggesting other mechanisms being at play during the diffusion process requiring further research. For the $z$-direction, saturation is reached after approximately 27 hours of immersion, while the $x$ and $y$ samples are saturated after approximately 170 hours.

The water uptake percentage at saturation is consistent for each direction and lies around 0.9% with respect to the dry (reference) state of the samples. The fibre weight percentage for the 50-ply panel was determined at 71.0% and with 2.4% of sizing and stitches (same fabric as used in [6]), the resin accounts for 26.6% in weight of the laminate. Assuming that glass fibres are impervious to water and water diffuses in the resin material only, and taken that for neat resin a water uptake percentage of 3.4% was found at saturation in [6], the expected uptake for the composite samples would be $0.266 \cdot 3.4\% = 0.90\%$, similar to the experimental values.

3. Numerical Modelling

3.1. Motivation

In order to further understand the mechanisms that cause the experimentally measured diffusivity to show a markedly anisotropic behaviour, a numerical modelling approach is adopted in this work. In this work, it is considered that the diffusion can be modelled as orthotropic, being fully described by a diagonal diffusivity matrix $D$ with three independent diffusivity values, $D_x$, $D_y$ and $D_z$, with the latter being the diffusivity along the fibres.

Here, it is hypothesised that such orthotropic behaviour is a consequence of the inhomogeneous microscopic structure of the composite material. Therefore, the diffusivity values are obtained through a steady-state diffusion analysis at the microscale:

$$D \nabla^2 c = 0 \tag{2}$$

where $\nabla^2$ is the Laplace operator, $c$ being the water concentration and $D$ is now a scalar since the microstructural components (fibres and resin) are isotropic.

3.2. RVE Model

The microscopic Representative Volume Element (RVE) considered in this work is a three-dimensional representation of unidirectional fibres and surrounding matrix, with the fibres aligned in the $z$ direction. Geometrically periodic RVEs with pseudo-random fibre distributions are generated using the discrete element software Hades. The two-dimensional geometry is meshed with 3-node triangles using Gmsh. Examples of RVEs with 1, 16 and 49 fibres can be seen in Figure 2. Lastly, since the RVE must be three-dimensional in order to consider the diffusion process along the fibres ($z$ direction), the 2D RVEs used as input are extruded at runtime and the 3-node triangles are replaced by 6-node wedge elements.

In order for the RVE to consistently represent a macroscopic material point, periodic water concentration boundary conditions are enforced in a similar way to what was done in [7] for
heat conduction. For each direction \((x, y, \text{ and } z)\), the difference in concentration for nodes on opposing surfaces is equal to a prescribed concentration gradient value. Additionally, in order to guarantee that the steady-state problem will have a unique solution, the volume average of the concentration in the whole RVE is equal to a prescribed value, which represents the concentration of the macroscopic material point represented by the micromodel. Figure 3(a) shows the concentration gradients which can be prescribed and Figure 3(b) shows an example of the obtained concentration field when unitary gradients are applied in every direction and the average concentration is fixed at zero. It is important to note that the model is only executed on the resin elements, as it is considered that water does not diffuse into glass fibres.

![Figure 2. Examples of generated RVEs with different number of fibres](image)

![Figure 3. Concentration gradients applied as boundary conditions and resultant concentration field](image)

After the steady-state solution is found, the volume average in the RVE of each flux component is computed, which would effectively represent the resultant macroscopic flux corresponding to the applied concentration gradients. Since the micro analysis is linear, applying unit concentration gradients in every direction results in flux values equal to the desired homogenised diffusivities.

Such formulation accounts for the diffusivity anisotropy caused by the geometric inhomogeneity (i.e. glass fibres acting as barriers for the water) [3]. However, literature evidence [4] suggests that diffusion may happen faster around the fibres when compared to bulk resin.
regions. In order to take this effect into account, a level set field is generated in order to describe
the distance of any point in the mesh to the surface of a fibre. This distance is then used to
determine the diffusivity of a point by linearly interpolating between a lower bound representing
the diffusivity in the bulk (unmodified) resin ($D_{bulk}$) and an upper bound representing the
diffusivity at the fibre-matrix interface ($D_{max}$). An example of the resultant diffusivity field can
be seen in Figure 4 for an interphase width of 2$\mu m$.

![Diffusivity field considering an interphase width of 2$\mu m$.](image)

3.3. Numerical Results
The numerical strategy discussed in the previous sections was used in an attempt to reproduce
the obtained experimental results. The RVE used in the analyses had 36 fibres with a diameter
of 15$\mu m$, a fibre volume fraction of 0.54 and a total cell size of 0.11x0.11x0.11 mm$^3$. The mesh
consisted of wedge finite elements with characteristic length of 0.5$\mu m$ in the x-y plane, so that
an interphase layer of 1$\mu m$ thickness would correspond to two element layers. Furthermore, in
order to allow for a smoother diffusivity variation as the distance to the nearest fibre increases,
a total of 81 integration points was used per finite element. The input bulk diffusivity value of
0.724 $\mu m^2/s$ for neat resin was obtained from previous experiments [6].

For the first model (No interphase), the level set fields were not used and the bulk diffusivity
was used at every material point. Therefore, only the effect of geometric inhomogeneity was
taken into account in this case. As expected, the homogenised transverse diffusivities were lower
than the neat resin value, due to the barrier effect caused by the fibres. On the other hand, in
the z direction, no obstacles are present and the homogenised value is equal to the neat resin
one. Compared with experimentally obtained results, the diffusivities provided by the model
are approximately 37% lower for $D_x$ and $D_y$ and 44% lower for $D_z$, suggesting the presence of
additional mechanisms that accelerate the water movement inside the composite material.

The next two models included interphase modelling by using level set fields, with the
interphase thickness $t_{int}$ and maximum diffusivity $D_{max}$ values being obtained from the work
of Joliff et al [4], where the authors propose that water moves approximately 5 times faster
in the interphase region. The thick interphase model considers a region of highly modified
material properties of 4$\mu m$ thickness based on MTA measurements, while the thin interphase
model considers a thickness of 1$\mu m$ based on AFM results reported in [4]. As expected, the
inclusion of an interphase yields higher homogenised diffusivity values. For both cases, however,
the obtained values were higher than the experimental ones. Such disagreement may be due to
differences in experimental aspects such as resin system, commercial fibre sizing, manufacturing
**Table 1.** Comparison between experiments and numerical simulations.

|                  | $D_{\text{bulk}}$ | $D_{\text{max}}$ | $\frac{D_{\text{max}}}{D_{\text{bulk}}}$ | $t_{\text{int}}$ | $D_x$  | $D_y$  | $D_z$  |
|------------------|-------------------|-------------------|---------------------------------------|------------------|--------|--------|--------|
| Experimental     |                   |                   |                                       |                  |        |        |        |
| No interphase    | -                 | -                 | -                                    | -                | -      | -      | 0.500  |
| Thick interphase [4] | 0.724           | 3.619             | 5.0                                  | 4.0              | 1.221  | 1.223  | 2.269  |
| Thin interphase [4] | 0.724           | 3.619             | 5.0                                  | 1.0              | 0.732  | 0.728  | 1.209  |
| Fit w/ thick interphase | 0.724          | 1.375             | 1.9                                  | 4.0              | 0.526  | 0.531  | 1.071  |
| Fit w/ thin interphase | 0.724         | 2.111             | 2.9                                  | 1.0              | 0.528  | 0.531  | 0.957  |

and curing processes, as well as in modelling choices such as fibre distribution and mesh size, among others.

For the two final models, the interphase thickness values obtained by Joliff et al [4] were kept and $D_{\text{max}}$ was adjusted to fit the experimental values. As the experimentally measured ratio between $D_x$ and $D_y$ differs from the one obtained for this particular RVE, $D_y$ was chosen as the one to be fit exactly, while a difference still remains in $D_x$. For the thick interphase model, the value obtained for $D_{\text{max}}$ was approximately twice as high as the bulk value, while for a thin interphase a value 3 times higher than $D_{\text{bulk}}$ was obtained. It is worth noting that neither model was able to correctly predict $D_z$, with an error of 26% for a thin interphase and of 18% for a thick interphase. This suggests that a combination of geometric inhomogeneity and linearly increasing diffusivity at the interphase are not enough to explain the observed differences in diffusivity. Further investigation is needed to elucidate the matter.

4. Conclusion

This work investigated the anisotropic diffusion behaviour observed in unidirectional glass/epoxy composite specimens through the coupling of experimental observations and numerical modelling. The experimental procedure consisted of manufacturing a 50-ply composite panel and cutting slices along its three planes of orthotropy. The slices were polished, dried to a moisture-free state and subsequently immersed in demineralised water at 50°C while having their water uptake measured at regular intervals. The process was modelled using a 3-dimensional RVE of the material representing a material point of a specimen during the transient phase of the diffusion phenomenon. Periodic concentration boundary conditions and a mass balance constraint were applied to the RVE and the diffusivity in each direction was measured by applied unit concentration gradients to the cell.

For experimental data, similar water uptake behaviour was observed for samples in the $x$ and $y$ direction due to a comparable fibre arrangement. A proper fit according to Fick’s law was obtained for these directions, while this was not possible for the samples in $z$ direction. Further research is necessary into the additional mechanisms playing a role for diffusion along the $z$ direction. For each direction the water uptake percentage at saturation reached up to 0.90%, which is in line with the expected uptake when considering the fibre weight percentage of the panel. The $z$ samples were fully saturated after immersion for about 27 hours, while the $x$ and $y$ samples required about 170 hours to reach full saturation, suggesting a strong dependency of the diffusion behaviour on the fibre orientation.

Results from the proposed numerical models show that the geometric effect of fibres acting as barriers for the water movement is indeed responsible for part of the observed anisotropy,
with the homogenised diffusivities in the $x$ and $y$ direction being approximately 2.2 times slower than in the $z$ direction. However, it was not possible to fit the experimental values by using only the bulk epoxy diffusivity, as the model still provided values approximately 40% lower than the ones observed experimentally. Lastly, level set fields are used to allow faster diffusion along the fibre-matrix interphase. Using the interphase thickness values measured by Joliff [4], a fit for the transverse diffusivity values was obtained. However, a fit for all three directions could not be obtained with the current micromodel.

Acknowledgements
The authors acknowledge the contribution of the TKI-WoZ and IRPWND projects for motivating and partly funding this research and of the TKI-MIMIC project industrial partners for providing useful feedback.

References
[1] Maxwell A S, Broughton W R, Dean G and Sims G D 2005 Review of accelerated ageing methods and lifetime prediction techniques for polymeric materials Tech. rep. National Physical Laboratory (NPL)
[2] Gautier L, Mortaigne B and Bellenger V 1999 Composites Science and Technology 59 2329
[3] Choi H S, Ahn K J, Nam J D and Chun H J 2001 Composites Part A: Applied Science and Manufacturing 32 709
[4] Joliff Y, Rekik W, Belec L and Chailan J F 2014 Composite Structures 108 876
[5] 2006 Technical data sheet - EPIKOTE resin MGS RIMR 135 and EPIKURE curing agent MGS RIMH 134-RIMH 137 Tech. rep. Momentive
[6] Rocha I B C M, Rajmaekers S, Nijssen R P L and van der Meer F 2015 20th International Conference on Composite Materials.
[7] Ozdemir I, Brekelmans W A M and Geers M G D 2008 International Journal for Numerical Methods in Engineering 73 185