DIFFUSION PROPERTY PREDICTION METHODS FOR NATURAL FIBRE KENAF COMPOSITE MATERIALS

Edward Dean Carman

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DECLARATION

I declare that this research report is my own unaided work. It is being submitted for the degree of Master of Science in Engineering at the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination at any other university.

(Edward Dean Carman)

<u>19th</u> day of <u>September</u> (year) <u>2014</u>

ABSTRACT

Five methods for predicting composite diffusion coefficients of unidirectional composite materials – the resistance analogy of Shen and Springer, the finite element unit cell method of Kondo and Taki, and the three-phase, four-phase and self-consistent models of Gueribiz et al. – were compared to experimental data for multi-directional kenaf fibre composites using three different thermoset resin systems: epoxy, polyester and vinylester, and one thermoplastic matrix: polypropylene.

These five methods were formulated to describe composites with unidirectional fibres, where diffusion occurs perpendicular to the fibre direction. They significantly underpredict the diffusion properties of multidirectional kenaf composite material. A new model, the bidirectional fibre model, was created to account for multidirectional fibre orientation. This model included an empirical fibre direction coefficient, F_D , to account for multidirectional fibre structures. The bidirectional fibre model, using a value of $F_D = 0.0069$ for needle-punched kenaf mat, was found to improve significantly the predicted thermoset composite diffusion coefficients.

None of the prediction methods, however, adequately described behaviour of the polypropylene-kenaf composite. The polypropylene matrix is essentially impermeable and the experimental data indicates that there may be some fibre volume fraction (11% in this case) below which no moisture absorption will occur. Polypropylene-kenaf composite moisture absorption may be better described by different prediction methods, such as percolation theory, rather than diffusion. This was not, however, investigated further in this research.

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LIST OF SYMBOLS AND ABBREVIATIONS

Symbol	Description						
$\langle i \rangle$	Volume average of <i>i</i>						
α	Thermal diffusivity; parallelepiped diffusion relation constant						
α_{fv}	Four-phase model constant						
α_{mv}	Four-phase model constant						
β	Finite element unit cell method randomness factor; parallelepiped diffusion relation constant						
ζ	Space coordinate along third principal axis						
η	Space coordinate along second principal axis						
ξ	Space coordinate along first principal axis						
ρ	Density						
$ ho_f$	Fibre density						
$ ho_m$	Matrix density						
$ ho_w$	Water density						
Φ	Four-phase model constant						
arphi	Thermodynamic potential						
Ψ	Four-phase model constant						
ψ	Three-phase model constant						
Α	Area						
A_L	Park's model constant						
B _D	Constant for resistance analogy, bidirectional fibre method						
B_L	Park's model constant						
B_W	Constant for modified resistance analogy						
С	Concentration of the diffusing substance						

Symbol	Description
C ₀	Initial concentration
c _p	Specific heat capacity
Cs	Surface concentration
C _{sat}	Saturation concentration
$C_{sat,c}$	Composite saturation concentration
C _{sat,f}	Fibre saturation concentration
C _{sat,m}	Matrix saturation concentration
D	Diffusion coefficient
D _c	Composite diffusion coefficient
D _e	Equivalent homogeneous diffusion coefficient
D_f	Fibre diffusion coefficient
D_m	Matrix diffusion coefficient
D_1, D_2, D_3	Diffusion coefficients along principal composite axes
D_x, D_y, D_z	Diffusion coefficients in x , y and z directions
F	Diffusion flux
f(x)	Concentration distribution function, general placeholder function
F _D	Fibre direction coefficient
K _a	Park's model constant
K_H	Park's model constant
k	Thermal conductivity, four-phase model constant
l	Plane sheet thickness
l_x, l_y, l_z	Thicknesses in x , y and z directions
m_0	Sample dry mass
m_t	Mass of diffusing substance absorbed by a sample in time, t

Symbol	Description
M_{∞}	Saturation mass absorption, relative to dry mass
M _t	Mass of diffusing substance passing a boundary in time, t , relative to dry mass
<i>M</i> *	Normalised mass absorption
Q	Heat flow, mass flow
q	Heat flux
r _f	Fibre radius
r_m	Matrix radius
r_v	Void radius
Т	Temperature
t	Time
t^*	Diffusion Fourier number
V	Volume
$v_{f,\parallel}$	Volume fraction of fibres parallel to diffusion direction
$v_{f,\perp}$	Volume fraction of fibres perpendicular to diffusion direction
v_f	Fibre volume fraction
v_v	Void volume fraction
W	Wetness fraction
W_{f}	Fibre mass fraction
x	Space coordinate normal to the diffusion/heat conduction section
	Symbol M_{∞} M_t M^* Q q r_f r_w T t V $v_{f, \parallel}$ v_f v_v w W_f x

Abbreviation	Description
EP	Ероху
FE	Finite element
GFR	Glass fibre reinforced
GRG	Generalised reduced gradient
LS	Least-squares
MAPP	Maleated polypropylene
NFR	Natural fibre reinforced
PALF	Pineapple leaf fibre
PP	Polypropylene
RH	Relative humidity
RVE	Representative volume element (unit cell)
SSE	Sum of squares of errors
UP	Unsaturated polyester
VBA	Visual Basic for Applications
VE	Vinylester

1 INTRODUCTION

Natural fibre reinforced (NFR) composite materials consist of fibres, derived from natural sources, embedded in a plastic matrix. The natural fibres are classified based on their origin as plant-, animal- or mineral-derived [1]. Wool and silk are examples of animal-derived fibres, while asbestos is an example of a mineral-derived fibre. The majority of current technical composites, however, use plant-derived fibres, such as flax or kenaf.

Natural fibre composites were in technical use over one hundred years ago with paper or cotton being used as reinforcement in pipes, sheets and tubes for electrical use, while some aeroplane fuel tanks and seats were also made with natural fibres and polymer binders [1]. The low cost and improved properties of other reinforcement materials led to a decline in the use of natural fibre composites in Western Europe, although India continued to produce jute-polyester pipes, pultruded profiles and panels [1].

By the start of the twenty-first century, there was a resurgence in use of natural fibre composites, particularly in the automotive sector with Mercedes-Benz [1,2]. Today, many other major automotive manufacturers, including BMW, Opel, Hyundai, Kia, Ford and Volkswagen, are also using these materials in their vehicles [3]. Examples of components made using natural fibre composites include: door panels, instrument panels, seat back panels, headliners, boot liners and various injected moulded parts from recycled thermoplastic composites. Figure 1.1 shows some of the natural fibre composite parts in a Mercedes S-Class.



a. Mercedes natural fibre composite parts [4]



b. Injection moulded handle from recycled
 PP-natural fibre granulate [3]

Figure 1.1 Examples of natural fibre composite car parts

Natural fibre composites have been progressively replacing E-glass fibre reinforced composites (GFR), compared to which they have similar specific material properties [2] and a number of economic advantages, such as lower costs. Typical 2011 market prices

for kenaf fibres are around US\$500-700/ton, while those for E-glass fibres are around US\$1000-2000/ton [5,6]. They also have lower tool wear and easier processing due to less abrasive fibres [1,2].

Natural fibre composites present a number of environmental advantages over their glass fibre counterparts:

- Lower production energy. Glass and glass fibres production is energy intensive, due to the high processing temperatures required. This energy is derived mainly from non-renewable sources. Natural fibres rely on solar energy to grow and only small amounts of fossil fuel energy are required for their extraction and processing. Consequently, their non-renewable energy requirements for production are 5-10 times lower than those for glass fibres. One kilogram of glass fibre mat requires 55 MJ of energy, compared to 10 MJ for flax and 15 MJ for kenaf [2,7].
- Substitution of matrix by higher natural fibre volume fraction. NFR components have higher fibre volume fractions than GFR components, for equivalent strength and stiffness properties. As a result, lower amounts of the base polymer matrix material are used. Epoxy resin requires around 141 MJ/kg of production energy and polypropylene 77 MJ/kg. The CO₂, CO, SO_x, and NO_x emissions associated with polymer production are also many times higher than those associated with natural fibre productions [7].
- *Reduced component weights.* NFR automotive components have been shown to be around 25% lighter than equivalent GFR components, resulting in improved fuel economy and lower emissions throughout the vehicle lifecycle [7].
- Energy and carbon credits from end of life incineration. Unlike GFR components, NFR components may be incinerated at the end of their lives, producing useable energy. The energy credit associated with the incineration of fibre is around 14 MJ/kg, while the lower polymer matrix fractions reduce emissions [7]. The net CO₂ emission addition from the incineration of natural fibres is theoretically zero, since the CO₂ released was sequestered by the plants during their growth [1,7].

Finally, the growth of natural fibres offers social benefits to developing economies, such as the Eastern Cape province of South Africa. Fibre plants, such as kenaf, are high-yield, low-maintenance, drought-tolerant crops that can be harvested within three to four months of planting, making them useful rotation crops and a source of employment for emergent farmers [8].

1.1 Plant fibres

1.1.1 Structure

Plant fibres are composed predominantly of cellulose, lignin and hemicellulose. The fibres used in composites consist of bundles of elementary fibre cells and are classified as bast (stem), leaf or seed/fruit fibres, depending on the part of the plant from which they are obtained. Typical examples of bast fibres are: jute, flax, kenaf, hemp and ramie; typical examples of leaf fibres are: sisal, henequen and pineapple leaf fibre (PALF); and typical examples of seed/fruit fibres are: cotton, coir and capok [2].

The schematic cross-section through a typical plant stem, in this case flax, is shown in Figure 1.2. Fibre bundles are surrounded by bast tissue and bonded to it with pectin [9]. The bundles themselves are composed of elementary fibre cells bonded with pectins and lignins. Waxes, composed of fatty acids, may be found on the surface of the fibre bundles [10].



Figure 1.2 Schematic of flax stem cross-section and fibre bundle (after [9,10])

A typical plant fibre cell, shown in Figure 1.3, has an outer wall of rigid cellulose microfibrils cross-linked with hemicellulose and embedded in lignin, and three inner walls of helically arranged microfibrils, also linked with hemicellulose and embedded in lignin [1,9,10,11].



Figure 1.3 Structure of a typical plant natural fibre cell [11]

The relative amounts of the materials vary by species of the fibres and will also vary within a species, depending on factors such as plant age, growing conditions and processing conditions [2,1,12]. Representative compositions of some fibres are shown in Table 1.1.

Fibre	Cellulose	Lignin	Hemicellulose	Pectin	Wax	Moisture content	
Bast							
Jute	61 – 71.5	12 – 13	13.6 - 20.4	0.2	0.5	12.6	
Flax	71	2.2	18.6 - 20.6	2.3	1.7	10	
Hemp	70.2 - 74.4	3.7 – 5.7	17.9 - 22.4	0.9	0.8	10.8	
Ramie	68.6 - 76.2	0.6 - 0.7	13.1 – 16.7	1.9	0.3	8	
Kenaf	31 – 39	15 – 19	21.5				
Leaf	•						
Sisal	67 – 78	8.0 - 11.0	10.0 - 14.2	10	2	11	
PALF	70 - 82	5-12				11.8	
Henequen	77.6	13.1	4 - 8	—	—		
Seed							
Cotton	82.7	—	5.7		0.6	—	
Fruit							
Coir	36 - 43	41 - 45	0.15 - 0.25	3-4		8	

 Table 1.1
 Chemical composition of some natural fibres (after [2])

1.1.2 Properties

The mechanical properties of natural fibres vary greatly due to their varying compositions, though fibres with higher cellulose content and smaller spiral angles tend

to have higher strength and stiffness values [2]. Some comparative fibre properties are shown in Table 1.2.

Fibre	Density	Diameter	Tensile strength	Young's	Elongation at
	[g/cm ³]	[µm]	[MPa]	Modulus	break [%]
				[GPa]	
Bast					
Jute	1.3-1.45	25-200	393–773	13-26.5	1.16-1.5
Flax	1.5	—	345-1100	27.6	2.7 - 3.2
Hemp	—	—	690	—	1.6
Ramie	1.5	—	400-938	61.4–128	1.2 - 3.8
Leaf					
Sisal	1.45	50-200	468-640	9.4-22.0	3-7
PALF	—	20-80	413-1627	34.5-82.51	1.6
Seed					
Cotton	1.5-1.6	—	287-800	5.5 - 12.6	7.0 - 8.0
Fruit					
Coir	1.15	100-450	131–175	4–6	15-40
Man-made					
E-glass	2.5	—	2000-3500	70	2.5
S-glass	2.5	—	4570	86	2.8
Aramid	1.4	—	3000-3150	63–67	3.3 – 3.7
Carbon	1.7	—	4000	230-240	1.4 - 1.8

 Table 1.2
 Comparative properties of some natural and man-made fibres (after [2])

The cellulosic structure of natural fibres makes them hydrophilic, causing them to absorb significant amounts of water. Fibres such as jute and agave absorb 25-35% of their mass when exposed to high moisture environments [13,10]. This moisture absorption causes hygroscopic swelling of the fibres, a reduction of their mechanical properties, and degradation and decomposition of the fibres over time. The swelling of the fibres in turn leads to degradation and damage of the overall composite material [2,14].

1.1.3 Extraction and processing

The fibrous parts of the plant are extracted using processes such as traditional retting; chemical or enzymatic retting; or mechanical extraction. Traditional retting processes, namely dew retting and water retting, use environmental bacteria and fungi to consume

the non-cellulosic tissues and separate the fibres from the core. Dew retting involves spreading the plant stalks over a grassy field where exposure to sun, air, dew and natural organisms causes fermentation, dissolving the stem material. Water retting processes submerge the plants in water where the combination of bacterial action and hygroscopic swelling separates the fibres. Retting time is carefully controlled – too little time results in poor separation; too much in degradation of the fibres themselves [15].

Chemical retting is more commonly used in industrial extraction where alkalis, mild acids and enzymes are used for fibre extraction. Sodium hydroxide is most commonly used, while sulphuric and oxalic acids, in combination with a detergent, are also used. Enzymatic extraction uses enzymes such as pectinase, hemicellulases and cellulases with pre- or post-chemical treatment [12].

Mechanical processes, such as decortication and steam explosion, physically separate the plant components [12]. Decortication uses hammer mills, cutter heads or crushing rollers to break up the plant material and separate the fibres. The use of ball mills has also been investigated [16]. In steam explosion processes, the plant stalks are exposed to steam and additives at high pressure and temperature for a short duration before being subjected to explosive decompression to separate the fibres[1].

The hydrophilic nature of natural fibres and the presence of waxy substances on their surface result in poor surface wetting and poor bonding of untreated fibres to most common hydrophobic resin systems. This reduces the mechanical properties of natural fibre composite materials and increases water absorption [2,12]. In order to address this, a number of fibre surface treatments are used.

The fibre treatments are broadly divided into physical methods that change the structural and surface properties of the fibres, without greatly affecting their chemical composition, and chemical treatment methods that modify the fibres by introducing a third material that is compatible with both the fibre and the matrix [1].

An example of physical modification is alkali treatment or mercerisation where the fibres are reacted with an alkali such as sodium hydroxide. This removes some of the lignin, wax and oils from the fibre surface and depolymerises the cellulose structure [2], improving the tensile properties of the fibre [1]. The surface roughness is increased and fibrils are formed, increasing the number of sites for resin/fibre mechanical interlocking and promoting increased resin/fibre interlocking at the surface. This improves the overall fibre-matrix adhesion [2].

Chemical methods improve the fibre-matrix bond in a number of ways. The surface tension is changed, bringing the surface energy closer to that of the matrix and improving

wettability [1,2]. If treatment agents with a low viscosity are used, the reinforcing fibres are impregnated with the compatible material, though lack of suitable solvents limits this to only certain matrix materials [2]. Finally, the overall chemical bond between fibre and matrix is improved by using a coupling agent capable of bonding to both the fibre and matrix material.

Examples of chemical methods to improve bonding include graft copolymerisation where the fibre is treated with a solution that is compatible with the matrix material e.g. vinyl monomers such as methyl acrylate. This forms a copolymer on the fibre surface that has properties characteristic of both the fibre and the grafted polymer [1,2]. The surface energy of the fibre is brought to a level closer to that of the matrix, improving wettability and interfacial adhesion [1].

A chemical method specific to natural fibre-polypropylene (PP) composites is treatment with maleated polypropylene (MAPP). This improves the surface characteristics of the fibre and promotes covalent bonding across the fibre-matrix interface [1]. The fibres may be pre-impregnated with MAPP before being chopped and melt blended with PP to form pellets for injection moulding [14], or else the blending of PP, MAPP and chopped fibres may be performed in a single extrusion step [17].

2 LITERATURE SURVEY

2.1 Basic diffusion relations

Diffusion is the process by which matter is transported from one part of a system to another by random molecular motion. Fick recognised that this was analogous to thermal conduction where heat is transported by random molecular motions [18].

The initial diffusion relationship described by Fick, known as Fick's First Law, states that the rate of transfer of a diffusing substance through a unit area of a section is proportional to the concentration gradient normal to that section, with the substance moving from areas of higher concentration to areas of lower concentration. For an isotropic substance with constant properties, this can be expressed as:

$$\mathbf{F} = -\mathbf{D}\frac{\partial \mathbf{C}}{\partial \mathbf{x}}$$
 2.1

where F is the rate of transfer of diffusing substance per unit area (diffusion flux), D is the diffusion coefficient, C is the concentration of the diffusing substance and x is the space coordinate normal to the sections [18].

This has a similar form to Fourier's First Law of heat transfer by conduction:

$$q = -k\frac{\partial T}{\partial x}$$
 2.2

where q is the rate of heat transfer per unit area (heat flux), k is the thermal conductivity of the material and T is the temperature.

The differential form of Equation 2.1, known as Fick's Second Law, in its most basic form, with one-dimensional diffusion and constant properties, is expressed as:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}$$
 2.3

This is comparable to Fourier's Second Law of heat conduction:

$$\frac{\partial T}{\partial t} = \frac{k}{c_p \rho} \frac{\partial^2 T}{\partial x^2}$$
 2.4

where c_p is the specific heat capacity and ρ is the density.

In the case where D depends on the concentration of the diffusing substance and also for non-homogeneous mediums where D can vary as a function of the spatial dimensions, Equation 2.3 can be expanded to:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial C}{\partial x} \right) + \frac{\partial}{\partial y} \left(D \frac{\partial C}{\partial y} \right) + \frac{\partial}{\partial z} \left(D \frac{\partial C}{\partial z} \right)$$
2.5

Finally, of interest for composite modelling, the Second Law may be arranged into a form that accounts for isotropic material properties by transforming the axes [18,19]:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial \xi} \left(D_1 \frac{\partial C}{\partial \xi} \right) + \frac{\partial}{\partial \eta} \left(D_2 \frac{\partial C}{\partial \eta} \right) + \frac{\partial}{\partial \zeta} \left(D_3 \frac{\partial C}{\partial \zeta} \right)$$
2.6

where, ξ , η , and ζ represent the three principal diffusion axes and D_1 , D_2 and D_3 are the principal diffusion coefficients along those axes. The similarity in form between Equations 2.5 and 2.6 is due to the fact that, by definition, the principal diffusivities vary only along the principal axes.

2.1.1 Analytical solutions to Fick's Law

Exact analytical solutions for transient thermal conduction with simplified boundary conditions and geometries have been presented in a number of sources [20] and have been adapted to suit diffusion problems [18]. A number of solutions, particularly relevant to absorption of moisture into a simple geometry, are presented here. The basic geometries are shown in Figure 2.1.



Figure 2.1 Basic one-dimensional diffusion geometries

Diffusion in semi-infinite media

The diffusion through the semi-infinite medium with initial, uniform concentration, C_0 , and constant surface concentration, C_s , shown in Figure 2.1a, is described in terms of the error function as [18]:

$$\frac{C(x,t) - C_s}{C_0 - C_s} = \operatorname{erf} \frac{x}{2\sqrt{Dt}}$$
2.7

where the initial concentration is $C(x, 0) = C_0$ and the surface concentration is $C(0, t) = C_s$.

The diffusion flux at the surface of the medium is given by:

$$F = -D \left. \frac{\partial C(x,t)}{\partial x} \right|_{x=0} = -\frac{D(C_0 - C_s)}{\sqrt{\pi Dt}}$$
2.8

The net amount of diffusing substance, m_t , entering or leaving the medium in a time, t, is given by integration of the flux with respect to time as:

$$\frac{m_t}{A} = -2(C_0 - C_s) \left(\frac{Dt}{\pi}\right)^{\frac{1}{2}}$$
 2.9

where A is the area through which diffusion occurs, and positive values of m_t indicate a net movement of substance in the positive x direction (entering the medium) and vice versa for negative values.

Plane sheet

The general solution [18,20] for a plane sheet (i.e. a medium bounded by two parallel planes), subjected to constant surface concentration on either side and with an initial concentration distribution described by f(x), shown in Figure 2.1b, is given in terms of infinite series as:

$$C(x,t) = C_{s,1} + (C_{s,2} - C_{s,1})\frac{x}{l} + \frac{2}{\pi}\sum_{n=1}^{\infty} \frac{(-1)^n C_{s,2} - C_{s,1}}{n} \sin\frac{n\pi x}{l} \exp(-n^2 \pi^2 t^*) + \frac{2}{l}\sum_{n=1}^{\infty} \sin\frac{n\pi x}{l} \exp(-n^2 \pi^2 t^*) \int_0^l f(x') \sin\frac{n\pi x'}{l} dx'$$
2.10

where the diffusion Fourier number, t^* , is given by Dt/l^2 , the initial concentration field is given by C(x, 0) = f(x) in the range 0 < x < l, and the surface concentrations are $C(0, t) = C_{s,1}$ and $C(l, t) = C_{s,2}$.

The specific case, applicable to many moisture absorption experiments, where the initial concentration distribution is uniform and the two surface concentrations are equal, may then be expressed as:

$$C(x,t) = C_s - \frac{4}{\pi} (C_s - C_0) \sum_{n=0}^{\infty} \frac{1}{2n+1} \sin \frac{(2n+1)\pi x}{l} \exp\{-(2n+1)^2 \pi^2 t^*\}$$
 2.11

where the uniform initial concentration is $C(x, 0) = C_0$ in the range 0 < x < l and the surface concentrations on either side are $C(0, t) = C(l, t) = C_s$.

The concentration of moisture, C, in a certain volume of material, V, is defined in terms of the mass of fluid in that volume, $m_{moisture}$, as:

$$C = \frac{m_{moisture}}{V}$$

This may be redefined in terms of the material bulk density, ρ_{solid} , and the dry mass of the volume, m_{solid} , by substituting the relation $V = m_{solid} / \rho_{solid}$

$$C = \rho_{solid} \frac{m_{moisture}}{m_{solid}} = \rho_{solid} M$$
 2.12

where $M = m_{moisture}/m_{solid}$ is the amount of moisture in a volume, relative to the dry mass. Alternatively, the initial mass of moisture in a body, $m_{moisture,0}$, may be subtracted to expressed the relation in terms of the net mass absorbed, $M = (m_{moisture} - m_{moisture,0})/m_{solid}$.

Using the above definitions for C and M, the net amount of diffusing substance, $M_t = M(t)$, that has entered the medium through both interfaces in time, t, is obtained by integrating Equation 2.11 over the wall volume (the full derivation is shown in APPENDIX A):

$$M_t = M_{\infty} \left[1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\{-(2n+1)^2 \pi^2 t^*\} \right]$$
 2.13

where M_{∞} is the saturation mass absorption, the amount of substance that has crossed the interfaces after infinite time, and is given by

$$M_{\infty} = \lim_{t \to \infty} M_t = \left\{ \frac{1}{2} (C_{s,1} + C_{s,2}) - C_0 \right\} / \rho_{solid} = (C_s - C_0) / \rho_{solid}$$

Although it is difficult to measure concentration directly, experimental results show good correlations between these analytical solutions and derived measurements, such as the total amount of diffusing substance absorbed [18,21,22].

Diffusion in a rectangular parallelepiped

The case of three-dimensional diffusion into a rectangular parallelepiped, under certain specific conditions, was solved analytically by Crank [18], based on the work of Carslaw and Jaeger [20] for heat transfer. The solution starts with the three-dimensional form of Fick's Second Law:

$$\frac{\partial^2 C}{\partial x_1^2} + \frac{\partial^2 C}{\partial x_2^2} + \frac{\partial^2 C}{\partial x_3^2} = \frac{1}{D} \frac{\partial C}{\partial t}$$
2.14

and applies it to the rectangular parallelepiped, shown in Figure 2.2 and defined by: $a_1 < x_1 < b_1, a_2 < x_2 < b_2, a_3 < x_3 < b_3$



Figure 2.2 Crank's parallelepiped diffusion geometry [18]

The solution consists of the product of the three one-dimensional solutions for diffusion along an axis, ($C_i(x_i, t)$ with i = 1,2,3):

$$\frac{\partial^2 C_i}{\partial x_i^2} = \frac{1}{D} \frac{\partial C_i}{\partial t}$$
 2.15

in the range $a_i < x_i < b_i$, with boundary conditions $\alpha_i \frac{\partial C_i}{\partial x_i} - \beta_i C_i = 0$ at $x_i = a_i$ and $\alpha'_i \frac{\partial C_i}{\partial x_i} - \beta'_i C_i = 0$ at $x_i = b_i$, and initial condition $C_i(x_i, t) = c_i(x_i)$ for t = 0, where α_i and β_i are constants.

The solution is only valid in cases where the initial conditions for the three-variable problem may be expressed as the product of the initial conditions for the one-variable cases i.e.

$$C(x_1, x_2, x_3, t = 0) = c_1(x_1)c_2(x_2)c_3(x_3)$$
2.16

The boundary conditions are then $\alpha_i \frac{\partial C}{\partial x_i} - \beta_i C = 0$ at $x_i = a_i$ and $\alpha'_i \frac{\partial C}{\partial x_i} - \beta'_i C = 0$ at $x_i = b_i$ and the solution is given by

$$C(x_1, x_2, x_3, t) = C_1(x_1, t)C_2(x_2, t)C_3(x_3, t)$$
2.17

Carslaw and Jaeger [20] showed that this solution is also applicable to anisotropic problems of the type described by Equation 2.6, provided the diffusion coefficients are constant and the bounding surfaces are perpendicular to the chosen axes.

For a parallelepiped with zero surface concentration and unit initial concentration, the solution is the product of three solutions of the type described in Equation 2.11. The reverse problem of unit surface concentration and zero initial concentration is obtained by subtracting this solution from unity. The case of a non-unity surface concentration is obtained by simple scaling and is given below for an anisotropic material [23] (note the length range has been shifted from $0 \le x_i \le l_i$ in Equation 2.11 to $-l_i/2 \le x_i \le l_i/2$):

$$C(x_{1}, x_{2}, x_{3}, t) = C_{s} \left[1 - \left(\frac{4}{\pi} \sum_{\substack{n=0\\\infty}}^{\infty} \frac{(-1)^{n}}{(2n+1)} \cos \frac{(2n+1)\pi x_{1}}{l_{1}} \exp \left\{ - \left(\frac{(2n+1)\pi}{l_{1}} \right)^{2} D_{1} t \right\} \right) \\ \times \left(\frac{4}{\pi} \sum_{\substack{n=0\\\infty}}^{\infty} \frac{(-1)^{n}}{(2n+1)} \cos \frac{(2n+1)\pi x_{2}}{l_{2}} \exp \left\{ - \left(\frac{(2n+1)\pi}{l_{2}} \right)^{2} D_{2} t \right\} \right) \\ \times \left(\frac{4}{\pi} \sum_{\substack{n=0\\n=0}}^{\infty} \frac{(-1)^{n}}{(2n+1)} \cos \frac{(2n+1)\pi x_{3}}{l_{3}} \exp \left\{ - \left(\frac{(2n+1)\pi}{l_{3}} \right)^{2} D_{3} t \right\} \right) \right]$$
2.18

where $-l_i/2 \le x_i \le l_i/2$ for i = 1,2,3; $C(x_1, x_2, x_3, t) = 0$ for $-l_i/2 < x_i < l_i/2$ when t = 0; and $C(x_1, x_2, x_3, t) = C_s$ on the surfaces where $x_i = \pm l_i/2$.

Using the mass absorption-concentration relation in Equation 2.12, the three-dimensional mass absorption may be derived and expressed in terms of the one-dimensional relations of Equation 2.13. This derivations is shown in APPENDIX A and gives:

$$\frac{M_t}{M_{\infty}} = 1 - \left(1 - \frac{M_{t,x}}{M_{\infty}}\right) \left(1 - \frac{M_{t,y}}{M_{\infty}}\right) \left(1 - \frac{M_{t,z}}{M_{\infty}}\right)$$
2.19

where $M_{t,x}$, $M_{t,y}$ and $M_{t,z}$ are the respective one-dimensional mass absorptions from Equation 2.13 in the x, y and z directions.

2.1.2 Modified analytical solutions to Fick's Law

The principal limitation of the foregoing analytical solutions based on Fick's Law is that they are unable to predict the depth of initial moisture penetration. For any time greater than zero, regardless of how small t is or how large x is, the solutions show that there will be a small, but non-zero, concentration throughout the medium. This would imply that penetrant molecules can reach deep parts of the medium almost instantly. This presents a problem if the goal of the modelling is to determine how long it takes moisture to penetrate to a certain depth in the medium e.g. to determine the insulating properties of a composite material [22].

Strain-dependent and gradient-dependent models

Frisch et al. [24] first addressed the problem by modifying Fick's model into a straindependent form by including a term based on the first derivative of the concentration with respect to the diffusion coordinate:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - \eta \frac{\partial C}{\partial x}$$
 2.20

where η is some constant that depends on the specific materials.

The solutions to this model for a semi-infinite medium and a plane sheet show an advancing moisture front [25]. The solution for the plane sheet is not, however, symmetrical about the centreline when the sheet is subjected to the same concentration boundary conditions on either side [21].

Tsai et al. [21] modified the relation in Equation 2.20 by splitting it into two parts, depending on the concentration gradient. For cases where diffusion occurs in the positive x-direction, Equation 2.20 remains as shown. When diffusion occurs in the negative x-direction, the sign of the second part of the equation is changed to positive. It predicts the location of the moisture front, but the accuracy of this prediction was not determined [21]. Experimental results for a plane sheet show that the gradient-dependent model provides a slightly better correlation for average concentration than Fick's Law. The gradient-dependent model requires prior knowledge of the diffusion direction in order to assign the correct sign to the gradient term. On basic geometries with simple boundary conditions, the diffusion direction can be determined by inspection. In more complex situations, however, it is not always possible to determine the diffusion direction beforehand and therefore the gradient-dependent model is unsuitable [22].

Advancing boundary model

The advancing boundary model by Chang et al. [22] removes the need to predetermine the diffusion direction. This model splits the diffusion into two parts: the first occurring before the advancing moisture front reaches the opposite side of the medium, and the second in the time after that. They defined a new constant, the Neumann constant, to describe the rate of advance of the moisture boundary. Experimental results showed a slightly better ($R^2 = 0.9991$ vs $R^2 = 0.9986$) correlation than pure Fick's Law diffusion.

2.2 Finite element methods

2.2.1 Thermal analogy for finite element solutions

The similarity between Fick's laws of diffusion and Fourier's laws of heat transfer, shown in §2.1, allows thermal finite element (FE) solvers and element technologies to be used to solve complex diffusion problems. The advantage of such an approach is that it allows the use of a commercial finite element modelling package such as ANSYS [26]. The most basic thermal-diffusion analogy sets $c_p \rho = 1$ and then directly maps the other variables as follows [18]:

Diffusion	Thermal
Diffusion flux, F	Heat flux, q
Concentration, C	Temperature, T
Diffusion coefficient, D	Heat transfer coefficient, k
1	^{<i>a</i>} Specific heat and density, $c_p \rho$

 Table 2.1
 Diffusion-thermal variable mapping

a. To facilitate subsequent structural analyses, ρ should be set to the actual material density. c_p should then be chosen to satisfy $c_p \rho = 1$

Diffusion boundary conditions may also be mapped to thermal boundary conditions as follows (note: the material through which diffusion or conduction occurs covers the area $x \le 0$, while the surrounding environment covers the area x > 0):

Diffusion	Thermal
Fixed concentration just within surface	Fixed temperature at surface
$C=C_{s}, x=0$	$T=T_{s}, x=0$
Diffusant flux	Heat flux
$F=F_{s}, x=0$	$q=q_{s}, x=0$
Impermeable surface	Adiabatic surface
F = 0	q = 0
Perfect contact between materials 1,2 with	Perfect contact between materials 1,2 with
interface concentrations of C_1 and C_2 and	interface temperatures of T_1 and T_2 and
interface fluxes of F_1 and F_2 respectively	interface fluxes of q_1 and q_2 respectively
$C_2 = PC_1 + Q$ (P,Q constant)	$T_1 = T_2$
$F_1 = F_2$	$q_1 = q_2$

Table 2.2Diffusion-thermal boundary condition mapping [18]

2.2.2 Limitations of the thermal analogy for finite element solutions

The thermal analogy provides a convenient method to solve diffusion problems using currently available thermal FE solvers, but is subject to some limitations, as listed below.

Coupled thermal-diffusion modelling

Since the temperature field is used to model concentration, it cannot be used to model temperature. It is thus not possible to solve a strongly coupled thermal-diffusion model (i.e. one in which the thermal and concentration fields are solved simultaneously, while influencing each other).

The thermal diffusivity, $\alpha = k/(\rho c_p)$, of many engineering materials is generally multiple orders of magnitude larger than their moisture diffusivity. It is thus possible to assume that the temperature field is at equilibrium at any time point on the diffusion timescale [27]. This allows the use of a weakly coupled solution method, whereby the temperature field is solved as a steady state for a specific time point and then used to determine the necessary material properties for the diffusion field.

Interface between dissimilar materials

In general, the concentration across the interface between two dissimilar materials is discontinuous, as described by the diffusion interface relation, $C_2 = PC_1 + Q$, given in Table 2.2. This discontinuity, illustrated in Figure 2.3, would have to be accounted for in any solution that formulates the problem in terms of *C* and would also present problems to many finite element solvers that need to solve a continuous field [28,29].



Figure 2.3 Discontinuous moisture concentration [29]

2.2.3 Modified thermal analogy to account for interface concentration discontinuity

The generally accepted approach to avoiding the discontinuity is to consider the relative concentration field. By noting that the thermodynamic potential, φ , should be continuous across the interface, a function, $f(\varphi) = C$, can be defined that allows the solution of C using a continuous formulation [28]. It is generally assumed that $f(\varphi)$ is linear, based on the saturation or equilibrium mass concentration of diffusant in the various materials at a given temperature and relative humidity. $f(\varphi)$ may then be rearranged to give what is variously known as the relative moisture concentration, normalised moisture concentration or 'wetness' fraction [28,29,30]. This is given as:

$$w = \frac{C}{C_{sat}}$$
 2.21

where w is the wetness fraction and C_{sat} is the saturated or equilibrium moisture concentration within the body under given temperature and humidity conditions.

Using the wetness fraction, the discontinuous concentration of Figure 2.3 becomes the continuous wetness fraction of Figure 2.4.



Figure 2.4 Continuous wetness fraction [29]

Using the wetness fraction approach, the Fick's Law equations become:

$$F = -DC_{sat}\frac{\partial w}{\partial x}$$
 2.22

$$\frac{\partial w}{\partial t} = \frac{DC_{sat}}{C_{sat}} \frac{\partial^2 w}{\partial x^2} = D \frac{\partial^2 w}{\partial x^2}$$
2.23

The thermal-diffusion variable mapping becomes that shown in Table 2.3.

 Table 2.3
 Diffusion-thermal variable mapping with wetness fraction

Diffusion	Thermal
Diffusion flux, F	Heat flux, q
Wetness, w	Temperature, T
Diffusion coefficient and saturated	Heat transfer coefficient, k
concentration, $D * C_{sat}$	
Saturated concentration, C _{sat}	^a Specific heat and density, $c_p \rho$

a. To facilitate subsequent structural analyses, ρ should be set to the actual material density. c_p should then be chosen to satisfy $c_p \rho = C_{sat}$

2.3 Diffusion property measurement

The two critical material properties governing moisture diffusion are the diffusion coefficient, D, and the saturation concentration, C_{sat} (the related equilibrium moisture absorption, M_{∞}). Both of these properties are most commonly determined using sorption experiments [18].

2.3.1 General sorption methods

Sorption methods involve measuring the total amount of diffusing substance absorbed by a medium in a given time. An advantage of these methods is that they do not require the direct measurement of variables such as concentration – something that is difficult to do in most solid materials.

The simplest sorption method involves suspending a dried sample in a moisture- and temperature-controlled environment (either fully submerged in a liquid or in a controlled humidity environment) and periodically weighing it to determine the amount of diffusing substance absorbed over time. A typical Fickian moisture uptake vs. square root of time curve is shown in Figure 2.5. The initial portion of curve ($t < t_L$) resembles diffusion into a semi-infinite medium and the slope is linear. The diffusivity and equilibrium moisture absorption for the specific conditions may be determined from the slope as follows [31]:

18

$$Slope = \frac{M_2 - M_1}{\sqrt{t_2} - \sqrt{t_1}} = \frac{4M_{\infty}}{l\sqrt{\pi}}\sqrt{D}$$
 2.24

The method gives an estimate of the combined quantity, $M_{\infty}\sqrt{D}$. In cases where the experiment has been run to equilibrium $(t > t_m)$, M_{∞} may be determined from direct inspection of the curve and *D* calculated accordingly. If it has not run to equilibrium, but there is sufficient additional data beyond the linear region $(t < t_L)$, both M_{∞} and *D* may be determined by non-linear curve fitting using the appropriate relation in §2.1.1. In the event that only data from the linear region is available, it is difficult to accurately separate *D* and M_{∞} [18].



Figure 2.5 Typical Fickian absorption curve (after [31])

Accounting for three-dimensional diffusion

The above relation is based on the one-dimensional form of Fick's law and assumes that diffusion occurs in one direction only. The specimens must be prepared taking this assumption into account. Generally, planar specimens are used whose length and width are significantly larger than their thickness, thus approximating an infinite sheet and reducing the impact of edge effects [18]. Edge effects may also be mitigated by sealing the edges of the specimen with a relatively impermeable material, such as metal foil [32]. Shen et al. [31] developed a method of compensating for edge effects by assuming that, in the earlier stages of diffusion ($t < t_L$), the absorption into each side of the plate is independent of the others and may be treated as absorption into a semi-infinite plate. The

overall absorbed mass is then given by summing the six individual absorbed masses. The diffusion coefficients are given by:

$$D = D_x \left(1 + \frac{l_x}{l_y} \sqrt{\frac{D_y}{D_x}} + \frac{l_x}{l_z} \sqrt{\frac{D_z}{D_x}} \right)^2$$
 2.25

where D_x , D_y , D_z are the diffusivities in the *x*, *y* and *z* directions and l_x , l_y , l_z are the sample thicknesses in those directions.

For a homogeneous material, the above equation reduces to

$$D = D_x \left(1 + \frac{l_x}{l_y} + \frac{l_x}{l_z} \right)^2$$
 2.26

Linear regression may also be applied to samples experiencing three-dimensional diffusion using Crank's parallelepiped solution [23].

The plane sheet absorption relation in Equation 2.13 assumes the diffusion coefficient is independent of concentration. If M_t is divided by M_{∞} , inspection of Equation 2.13 shows that the resulting normalised moisture absorption, M_t/M_{∞} , will be independent of M_{∞} and will vary from 0 for a dry specimen to 1 for a saturated speciment.

If curves of normalised moisture absorption versus time are plotted for specimens subjected to different relative humidities (i.e. different values of M_{∞}), the time taken to reach a given value of M_t/M_{∞} should not vary with relative humidity. If it does, it is likely the material properties are concentration-dependent.

Specific sorption methods for samples submerged in liquid

When measuring moisture uptake of a specimen in a humid environment, it is possible to enclose the weight measuring equipment within the environment (e.g. by suspending the samples from a spring of known stiffness and measuring deflection). Buoyancy effects make this method less accurate for samples submerged in a liquid. It is thus necessary to remove the sample from the liquid, wipe off any excess surface liquid, quickly weigh it and then return it to the liquid. This disrupts the diffusion process and it is difficult to wipe off surface liquid without removing some of the liquid inside the specimen. The result is that the measured weights are slightly scattered and the uncertainty in the calculation of the diffusing properties is increased [18].

In order to avoid the need to weigh a specimen, the relationship between concentration and hygric strain has indicated an alternative way of measuring moisture uptake [32]. Experiments have shown that the local in-plane hygric strain is generally related to concentration and varies with concentration in a predictable way [32,33]. For planar sorption experiment specimens, the surface strain varies in proportion to the global hygric strain, which in turn varies in proportion to the average concentration and mass uptake. The curve of surface strain vs. the square root of time thus has a similar form to the mass absorption curve of Figure 2.5. Tsai et al. [32] used this strain curve to predict diffusion coefficients in the same way as a mass absorption curve would be used.

Anisotropic materials

Sorption methods may be used to determine the diffusion coefficients for anisotropic materials. In this case, the planar samples are prepared in such a way that the diffusion direction coincides with one of the principal diffusion axes. The experiment then produces the value for the principal diffusion coefficient along that axis. Repeating the experiment with samples aligned along the remaining principal axes produces the remaining coefficients [18].

2.4 Moisture absorption in natural fibre composites

There have been a number of studies published on the moisture absorption behaviour of natural fibres and their composites. Bessadok et al. [10] studied the moisture absorption behaviour of agave fibres. They showed that the equilibrium moisture absorption follows Park's model:

$$M_{\infty} = \frac{A_L B_L a_w}{1 + B_L a_w} + K_H a_w + K_a a_w^n$$
 2.27

where a_w is relative humidity and A_L , B_L , K_H , K_a and n are model parameters.

They also determined diffusion coefficients based on the initial (D_1) and final stages (D_2) of sorption experiments and found them to depend strongly on the moisture concentration. Their researched values for the Park's model parameters for agave and listed values for alfa and flax are shown in Table 2.4, while the resulting plot is shown in Figure 2.6. Their measured values of D_1 and D_2 are shown in Figure 2.7.
Fibre	Agave	Alfa	Flax
A_L	0.015	0.013	0.021
B_L	(>50)	(>50)	47
K _H	0.016	0.012	0.011
Ka	0.47	0.61	0.25
n	8.4	10	18

 Table 2.4
 Bessadok et al.'s Park's model parameters for various untreated fibres [10]



Figure 2.6 Bessadok et al.'s fibre equilibrium moisture uptakes, from Park's model [10]



Figure 2.7 Bessadok et al.'s first half sorption (D_1) and second half sorption (D_2) diffusion coefficients [10]

Absorption studies conducted on natural fibre composites at room temperature show that they generally display Fickian absorption behaviour. Espert et al. [34] conducted tests on wood, sisal, coir and Luffa sponge fibre composites with a polypropylene (PP) base and showed Fickian behaviour at 23 °C, with slight deviations at 50 °C and 70 °C. Their results showed significant degradation of mechanical properties, such as Young's modulus and failure loads for saturated composites. Similar Fickian behaviour and material property degradation were shown by Arbelaiz et al. [35] for flax fibre-PP composites, Dhakal et al. [36] for hemp-polyester composites, and Akil et al. [37] for jute-unsaturated polyester composites; though the latter described them as pseudo-Fickian behaviour since their samples did not reach equilibrium, but did display Fickian absorption in the initial stages.

At elevated temperatures (above 70 °C), a number of studies have shown that natural fibre composites display non-Fickian absorption behaviour and further degradation of their material properties.

Chow et al. [14] immersed polypropylene-sisal composites in water at 90 °C and observed that the moisture absorption would reach a maximum value, after which the sample mass would start decreasing. They suggested that, since the polypropylene matrix is highly water resistant, the mass loss was due to the dissolution of lignaceous material and waxy substances from the sisal fibre surface. Their work also showed a degradation of stiffness and strength properties with increasing moisture content.

George et al. [38] showed increased water absorption with increasing temperature for pineapple fibre-low density polyethylene composites, as well as concentration dependence of the diffusion coefficient.

Weight loss at elevated temperatures has also been observed in traditional composite materials. Loos et al. [39] exposed E-Glass-PE composites to high humidity and temperature environments (air at 100% RH and 50 °C and 60 °C; water at 65 °C) and observed mass loss, as well as material flaking away from the resin, while Loos and Springer [40] exposed graphite-epoxy composites to saturated steam at 150 °C with similar results. In both cases, the effects were attributed to micro-cracking and degradation of the resin matrix, advanced by the elevated temperature [39], rather than dissolution of the fibres themselves.

2.5 Diffusion property prediction

During modelling, the macroscopic behaviour of a microscopically heterogeneous material, such as a composite, may be treated as a homogeneous analogue with equivalent (effective) macroscopic properties selected so that its behaviour with regard to certain parameters (e.g. moisture uptake, concentration profile etc.) is similar to that of the heterogeneous media [18].

2.5.1 Unit cell methods

Heterogeneous materials, like composites, generally have a microstructure that repeats throughout the material. This structure can be considered as a number of identical, repeating unit cells. Each unit cell contains material of the discrete and continuous phases and is representative of the overall structure of the material. A single unit cell may then be modelled using analytical or numerical methods, such as FEM, to determine its diffusion characteristics. These characteristics are then used to determine effective properties of the equivalent homogeneous unit cell [18].

Thermal resistance analogy

Shen and Springer [31] suggested a relation to determine the effective diffusion properties of a unidirectional composite material, based on Springer and Tsai's earlier work concerning the thermal conductivity of unidirectional composites [41]. This work considered the unit cell, shown in Figure 2.8a, and converted it to the equivalent series/parallel resistance network shown in Figure 2.8b, while applying equivalent diffusion fluxes to determine the effective diffusion coefficient normal to the fibre direction.





Assuming that the fibres have a circular cross section and are arranged in a square array, the effective composite diffusion coefficient, D_c , was expressed in terms of the fibre volume fraction, v_f , as:

$$\frac{D_c}{D_m} = 1 - 2\sqrt{v_f/\pi} + \frac{1}{B_D} \left[\pi - \frac{4}{\sqrt{1 - (B_D^2 v_f/\pi)}} \tan^{-1} \frac{\sqrt{1 - (B_D^2 v_f/\pi)}}{1 + B_D \sqrt{v_f/\pi}} \right]$$
2.28

where subscripts *m* and *f* refer to matrix and fibre properties respectively, $v_f < 0.785$, and

$$B_D = 2\left(\frac{D_m}{D_f} - 1\right)$$

Applying some simplifying assumptions for impermeable fibres, Shen and Springer [31] found a reasonable correlation between the predicted and experimentally obtained values for impermeable fibre graphite-epoxy composites at various fibre volume fractions. The relation does not, however, account for the discontinuous concentration field, described in §2.2.2, that usually occurs across the interface between two materials.

Modified resistance analogy

Kondo and Taki [30] addressed the problem of discontinuous concentration by formulating it in terms of the relative moisture concentration or wetness fraction. By using the correct thermal-diffusion analogy of $k \rightarrow DC_{\infty}$, rather than $k \rightarrow D$ as used by Shen and Springer, the effective coefficient, D_c becomes:

$$\frac{D_c}{D_m} = \left(1 - 2\sqrt{v_f/\pi}\right)\frac{C_{sat,m}}{C_{sat,c}} + \frac{C_{sat,m}}{C_{sat,c}}\frac{1}{B_W} \left[\pi - \frac{4}{\sqrt{1 - (B_W^2 v_f/\pi)}} \tan^{-1}\frac{\sqrt{1 - (B_W^2 v_f/\pi)}}{1 + B_W \sqrt{v_f/\pi}}\right]$$
2.29

where subscript, *sat*, refers to saturated/steady state conditions, $B_W = 2\left(\frac{C_{sat,m}D_m}{C_{sat,f}D_f} - 1\right)$ and the effective saturated concentration, $C_{sat,c}$, is defined as:

$$C_{sat,c} = C_{sat,f}v_f + C_{sat,m}(1 - v_f)$$
2.30

The results for the modified analogy did not, however, improve the agreement with experimental results for impermeable fibre composites [30].

Finite element unit cell

Kondo and Taki [30] then modelled unit cells of composite materials to get effective properties under steady state conditions for a composite with randomly distributed, impermeable unidirectional fibres. Their approach was to treat a random array of fibres as a square array of square cylinders of matrix embedded in a material with equivalent effective properties to a hexagonal array composite. The effective diffusion coefficient in the transverse plane of a transversely isotropic material was defined as

$$\langle F_i \rangle = -D_{e,i} C_{sat,c} \left\langle \frac{\partial w}{\partial i} \right\rangle$$
 2.31

where subscript, *i*, represents the specific principal axis, $D_{e,i}$, the effective diffusion coefficient along that axis, and < > denotes the volume average.

The divergence theorem was then used with the geometries shown in Figure 2.9b and Figure 2.10b, with boundary relative concentration, w(s) = y, to show that $\langle \frac{\delta w}{\delta y} \rangle = 1$, giving

$$D_{e,y}C_{sat,c} = -\langle F_y \rangle \tag{2.32}$$

The effective properties for the uniform hexagonal array composite, shown in Figure 2.9, were then calculated using Equation 2.32 and the wetness field obtained from the finite element model in Figure 2.9b.



Figure 2.9 Hexagonal array unidirectional composite [30]

The effective properties of the hexagonal array were then applied to the representative model of the random array composite shown in Figure 2.10. The degree of randomness is represented by β which is defined as the ratio of the side length of the square cylinders to the spacing distance between adjacent cylinders. The authors compared the model predictions to experimental results for impermeable fibre E-glass-epoxy composites and found reasonable agreement for values of $\beta = 0.5$ [30]. Their model did not account for the possibility of voids in the matrix and required one or more separate FE simulation runs for each fibre-matrix combination.



Figure 2.10 Representing a random array unidirectional composite with a combination of hexagonal array composite and resin regions [30]

Three-phase model

The three-phase model proposed by Gueribiz et al. [42] is based on the unit cell or representative volume element (RVE), shown in Figure 2.11, composed of reinforcing fibre, surrounded by matrix, in turn surrounded by the equivalent homogeneous medium whose properties are to be determined. A uniform diffusion flux, F, is applied to the boundary. The effective diffusion coefficient, D_c , is given by:

$$\frac{D_c}{D_m} = \frac{(1 - v_f) + \psi(1 + v_f)}{(1 + v_f) + \psi(1 - v_f)}$$
2.33

Where

$$\psi = \frac{C_{sat,f}}{C_{sat,m}} \frac{D_f}{D_m}$$
$$v_f = \frac{r_f^2}{r_m^2}$$



Figure 2.11 Representative volume element – three-phase model [42]

The authors showed good agreement between the three-phase model and numerical prediction approaches for square array impermeable fibre composites with $v_f < 0.5$ and hexagonal array composites with $v_f < 0.78$. Comparing the method to finite element predictions for permeable fibre composites with $\psi = 20$, they found good agreement across all volume fractions, especially so for $v_f < 0.5$. They did not, however, perform any comparison to experimental data for permeable fibre composites.

Self-consistent model

Gueribiz et al.'s [42] self-consistent model was formulated as an alternative to the threephase model and treats the material as a fibre surrounded by a matrix of the equivalent homogeneous medium, as shown in Figure 2.12. Using the same solution procedure as for the three-phase model, the effective diffusivity is given by:

$$\frac{D_c}{D_m} = \frac{1}{2} \left(\frac{D_f}{D_m} (2v_f - 1) + (1 - 2v_f) + \sqrt{\frac{4D_f}{D_m} + \left[\frac{D_f}{D_m} (1 - 2v_f) + (2v_f - 1)\right]^2} \right)$$
 2.34

The above relation is not valid for high values of v_f and low values of D_f/D_m (e.g. when $D_f = 0$ it is valid only for $v_f \le 0.5$). To avoid this problem, an iterative procedure that introduces a partial volume fraction at each step is used [43,42]. The partial volume fraction, $\Delta v_{f,n}$ at each step, *n*, is given by:

$$\Delta v_{f,n} = \frac{v_f}{N - (n-1)v_f}$$
 2.35

where *N* is the total number of iteration steps.

The effective diffusion coefficient at each iteration step, *n*, is given by:

$$\frac{D_{c,n}}{D_{c,n-1}} = \frac{1}{2} \left(\frac{D_f}{D_{c,n-1}} (2\Delta v_{f,n} - 1) + (1 - 2\Delta v_{f,n}) \right) + \frac{1}{2} \sqrt{\frac{4D_f}{D_{c,n-1}} + \left[\frac{D_f}{D_{c,n-1}} (1 - 2\Delta v_{f,n}) + (2\Delta v_{f,n} - 1) \right]^2}$$
2.36

where $D_{c,0} = D_m$

The authors compared the self-consistent model predictions for impermeable fibre composites to those of the three-phase model and showed that the two converged as the

number of iterations was increased. The requirement for an iterative procedure, however, rendered the self-consistent model less desirable for use as a closed-form solution.



Figure 2.12 Representative volume element – self-consistent model [42]

Four-phase model

Gueribiz et al. [42] noted that the three-phase and self-consistent models did not account for effects of voids in the composite and so created the four-phase model, that included a void layer between the fibre and matrix, as shown in Figure 2.13. The effective diffusion coefficient was then given by:

$$\frac{D_c}{D_m} = \frac{(1-kv_f)[1+k+\alpha_{mv}(\Psi/\Phi)(k-1)] + (1+kv_f)[\Phi(k-1)+\alpha_{mv}\Psi(k+1)]}{(1+kv_f)[1+k+\alpha_{mv}(\Psi/\Phi)(k-1)] + (1-kv_f)[\Phi(k-1)+\alpha_{mv}\Psi(k+1)]}$$
2.37

where

$$k = \frac{v_v + v_f}{v_f}, \ \Phi = \alpha_{mv} \frac{D_v}{D_m}, \ \Psi = \alpha_{fv} \frac{D_f}{D_m}, \ \alpha_{mv} = \frac{C_{sat,v}}{C_{sat,m}}, \ \alpha_{fv} = \frac{C_{sat,f}}{C_{sat,v}}, \ C_{sat,v} \text{ is the saturation}$$

concentration in the void, and v_v is the void volume fraction.



Figure 2.13 Representative volume element – four-phase model [42]

When $v_v = 0$, the four-phase model reduces to the three-phase model. They did not compare the four-phase predictions to numerical or experimental results.

2.6 Critical evaluation of diffusion property prediction methods

The diffusion coefficient prediction methods from the literature possess a number of shortcomings, which may make them insufficient for the prediction of the diffusion coefficients of composites where the fibres are highly permeable and are not uniformly arranged, such as kenaf fibre mat composites. These shortcomings are assessed for each of the methods below:

2.6.1 Saturation concentration

The definition of saturation concentration, Equation 2.30, given by Kondo and Taki [30] assumes that there are no void regions in the composite and also assumes that all regions in the composite are accessible to the diffusing substance. If there are void regions, the composite sample will contain more moisture than the relation suggests and the observed saturation concentration will be higher than predicted. If there are regions that are inaccessible to the diffusing substance, e.g. in the case of a material with an impermeable matrix that isolates some of the fibres, the test sample may appear to be saturated, but may still contain internal dry regions. These regions would lower the actual moisture content of the sample and result in experimental values that are lower than the predicted values.

2.6.2 Thermal resistance analogy

The thermal resistance analogy of Shen and Springer [31] assumes that that all the fibres lie perpendicular to the diffusion plane, are uniformly distributed in a grid arrangement and are completely surrounded by matrix. The method also assumes that the concentration field is not discontinuous at the boundary between dissimilar materials (as described in §2.2.2) and that there are no voids in the material. Their experimental work compared the prediction method to graphite-epoxy composites with near-impermeable fibres, but the method has not been compared to data for permeable fibre composites.

The assumption of a perpendicular fibre arrangement does not account for any fibres that may lie wholly or partially in the direction of diffusion. If such fibres were present in a composite, the fibres would increase the amount of substance diffusing through the composite and would result in this thermal resistance analogy under-predicting the diffusion coefficients.

By assuming that the fibres are uniformly distributed and surrounded by matrix, this method does not account for the possibility of fibres crossing over each other (providing a diffusion 'short circuit') or fibres coming into direct contact with the surrounding

medium. Where the actual composite has a non-uniform arrangement, the actual diffusion will be higher and the method may under-predict the composite diffusion coefficient.

Similarly, any voids in the composite will provide regions of low resistance to moisture flow that are not accounted for in the model and so may also lead to under-prediction of the diffusion coefficient

Finally, by assuming each fibre is completely surrounded by matrix, the model may lead to incorrect predictions in the cases where the matrix is impermeable. In these cases, the model predicts zero diffusion through the composite, regardless of the fibre volume fraction. If, as discussed in the previous paragraphs, there are other moisture paths present, the model will produce predictions that are lower than the actual values.

2.6.3 Finite element unit cell

Kondo and Taki's [30] Finite Element unit cell addressed some of the limitations of the resistance analogy: it accounts for the possibility of discontinuous moisture concentration at the fibre-matrix interface and partially accounts for non-uniformity in the fibre arrangement. It still, however, assumes that all fibres lie perpendicular to the diffusion plane (although their spacing is no longer constant) and, since the final unit cell of Figure 2.10 incorporates the initial cell in Figure 2.9, the model also still assumes the fibres are completely surrounded by matrix. The authors compared the model predictions to experimental results for impermeable fibre E-glass-epoxy composites and found reasonable agreement for values of $\beta = 0.5$ [30]. The method has not been compared to data for permeable fibre composites.

The unit cell method would be expected to experience similar problems with crossing fibres, voids and impermeable matrices as may be experienced by the resistance analogy. Finally, the model has the limitation that it does not produce a closed-form solution, but rather requires multiple finite element model iterations.

2.6.4 Three-phase model

The three-phase model proposed by Gueribiz et al. [42] accounts for the potential concentration discontinuity at the fibre-matrix interface by incorporating the material saturation concentrations. The model assumes that the fibres lie perpendicular to the diffusion plane, are uniformly arranged and that there are no voids in the composite. The authors showed good agreement between the three-phase model and numerical prediction approaches for square array impermeable fibre. They also compared the method to finite element predictions for permeable fibre composites and found good agreement across all

volume fractions. They did not, however, perform any comparison to experimental data for permeable fibre composite sample.

The three-phase model would be expected to experience similar limitations as the resistance method when used to predict the properties of composites with crossing fibres, non-uniform fibre arrangement, voids and impermeable matrices.

2.6.5 Self-consistent model

Gueribiz et al.'s [42] self-consistent model has a similar formulation to the three-phase model and would be expected to experience similar limitations. The authors compared the self-consistent model predictions for impermeable fibre composites to those of the threephase model and showed that the two converged as the number of iterations was increased. They did not assess its ability to predict the behaviour of permeable matrix composites. The requirement for an iterative procedure renders the self-consistent model less desirable for use as a closed-form solution.

2.6.6 Four-phase model

Gueribiz et al.'s [42] accounts for the effects of voids in the composite by including a void layer between the fibre and matrix. Aside from this void layer, the other underlying assumptions remain the same as for the three-phase model. They did not compare the four-phase predictions to numerical or experimental results and the model has not been compared to results for permeable fibre composites.

The four-phase model would be expected to experience similar limitations to the threephase model, but should be better able to account for situations where there are voids in the matrix.

2.6.7 Summary of limitations of current methods

The methods evaluated above possess a number of potential limitations should they be used for the prediction of the diffusion properties of natural fibre composites with nonuniform fibre arrangements. These limitations would generally be expected to lead to the under-prediction of the composite diffusion properties. Of the methods listed, only the resistance analogy of Shen and Springer [31] and Kondo and Taki's [30] Finite Element unit cell method have been compared to experimental data, and then only for composites with near-impermeable fibres. None of the methods have been compared to data from permeable fibre composites, so it not possible, based on the literature, to quantify the impact of the assumptions made when using the models to predict properties for natural fibre composites.

3 OBJECTIVES

3.1 Formulation of objectives

The lignocellulitic structure of natural fibres makes them hydrophilic and results in the fibres themselves absorbing a significant amount of moisture [10]. Additionally, the waxy surface of the fibres impedes proper bonding to the resin and may leave moisture paths in the composite [2,12]. Finally, the literature has shown that the physical properties of natural fibre composites, such as tensile strength, impact strength and flexural strength, are significantly degraded by long-term water absorption due to degradation of the fibres [34,35,44,37].

The diffusion of moisture into a composite may be modelled and predicted using the Fick's Law equations for simple cases, or finite element methods for more complex, general cases. Both methods rely on accurate predictions of composite bulk diffusion properties in order to obtain useful results.

Bulk diffusion properties may be simply obtained from mass absorption tests on composite samples [18]. The amount of time required to complete these tests, however, makes them unfeasible when considering the numerous matrix, fibre and volume fraction combinations that would be analysed during the initial design stages of a composite part.

The review of existing literature shows that there are a number of methods proposed to predict the bulk diffusion properties (effective diffusion coefficient and effective saturation concentration) of composite materials based on the diffusion properties of their constituent parts – most commonly the fibre and the matrix. These relations have predominantly been applied to composites reinforced by glass fibre [30] or carbon/graphite fibre [31]. The assumption is often made that the fibres are impermeable, in order to simplify the equations. A number of sources [30,31] have compared the predictions from these models to experimental data for composites with impermeable fibres, but none have done so for materials, such as natural fibre composites, where the fibres themselves absorb a significant amount of moisture.

Previous research at the University of the Witwatersrand has compared the moisture absorption of kenaf fibre composites made with various resin systems and manufacturing methods [45,46], but has not examined the detailed diffusion properties.

There is a need to compare the existing diffusion property predictions methods to diffusion properties derived from experimental data for multidirectional, permeable kenaf fibre composites.

3.2 Objectives

The overall object was to make use of existing experimental data generated by two previous researchers to compare existing prediction methods to experimental measurements. This was broken down as:

- Predict composite diffusion properties at various volume fractions using:
 - Shen and Springer's thermal resistance analogy [31].
 - Kondo and Taki's unit cell FE method [30].
 - Gueribiz et al.'s three-phase model [42].
 - Gueribiz et al.'s four-phase model, incorporating voids [42].
 - Gueribiz et al.'s self-consistent model [42].
- Compare predicted diffusion properties with experimental diffusion properties for kenaf-epoxy, kenaf-polyester, kenaf-vinylester thermoset composite samples from Rassmann [46] and kenaf-polypropylene thermoplastic composite samples from Asumani [45].
- Produce an additional prediction method to account for any observed variation between the existing prediction methods and the experimental data.

4 PROCEDURE AND METHODS

4.1 Outline of procedure and methods

Experimental diffusion property (D_c and $M_{\infty,c}$) values for kenaf-epoxy, -polyester and -vinylester thermoset composites were measured from absorption experiments carried out by Rassmann [46] and values for kenaf-polyester thermoplastic composite were measured from absorption experiments carried out by Asumani [45]. The experimental values of D_c and $M_{\infty,c}$ were compared to theoretical values of D_c and $M_{\infty,c}$ calculated using the five chosen prediction methods, with kenaf fibre (D_f and $M_{\infty,f}$) and epoxy, polyester, vinlyester and polypropylene matrix (D_m and $M_{\infty,m}$) diffusion properties as inputs.

The kenaf fibre diffusion coefficient (D_f) was measured from experimental tests carried out by Rassmann [46]. The kenaf saturation mass absorption $(M_{\infty,c})$ and the matrix diffusion properties $(D_m \text{ and } M_{\infty,m})$ for the three thermoset and one thermoplastic matrix were obtained directly from values listed in the literature.

The details of this process are expanded in the following sections. Where applicable, sample calculations are shown in APPENDIX B.

4.2 Obtaining composite diffusion coefficient (D_c) and saturation moisture absorption values $(M_{\infty,c})$

Composite diffusion coefficients, D_c , and saturation moisture absorption values, $M_{\infty,c}$, were obtained from the results of Rassmann [46] and Asumani [45], using the curve fitting procedure described in §4.2.1, below.

Rassmann performed absorption tests on 4x50x50mm kenaf composite samples with unsealed edges that were submerged in water at 23 °C. The samples were prepared from air-dried kenaf fibres using resin transfer moulding with a heated mould. A schematic of a typical sample is shown in Figure 4.1.

Nine samples were tested comprising three resin systems – epoxy, polyester and vinylester – and three fibre volume fractions – 15%, 22.5% and 30%. The initially dry samples were placed in water and their mass increase was measured after one hour. Thereafter, mass measurements were taken on a daily basis until the experiment was stopped after 28 days.

The absorption data gathered by Rassmann [46] for 22.5% volume fraction samples is shown in Figure 4.2. The graphs show Rassmann's experimental data points and the

curve that was fit through them. The method used to calculate the fitted curve is described in §4.2.1. Rassmann's complete data is given in APPENDIX B.



Figure 4.1 Schematic of typical rectangular diffusion test sample



Figure 4.2 Rassmann's [46] absorption data for 22.5% volume fraction samples and various resin systems, with fitted curves added in this work

Asumani [45] performed absorption tests on kenaf-polypropylene samples with sealed edges and thicknesses ranging from 1.8mm to 2.9mm, submerged in water at 23 °C. The samples were prepared from air-dried kenaf fibres and polypropylene pellets, compressed in a heated mould. A schematic of a typical sample is shown in Figure 4.1.

Four samples were tested with fibre weight fractions of 20%, 25%, 30% and 35%. The initially dry samples were placed in water and their mass increase was measured on a weekly basis for the first four weeks. Thereafter, mass measurements were taken every four weeks. The experiment was stopped after a total time of 48 weeks.

The absorption data gathered by Asumani [45] is shown in Figure 4.3, together with the curve fitted to it in this work.



• Asumani - Wf = 20%, t = 1.8mm
 × Asumani - Wf = 25%, t = 2.2mm
 + Asumani - Wf = 30%, t = 2.5mm
 △ Asumani - Wf = 35%, t = 2.9mm

Figure 4.3 Asumani's [45] absorption data for kenaf-polyester samples, with fitted curves added in this work

4.2.1 Procedure to determine fibre and composite diffusion properties using absorption calculations

Diffusion properties were determined by fitting a mass absorption curve $(M_t(D, M_{\infty}, t))$ to experimental measurements of moisture absorption over time.

Deriving the mass absorption curve function, $M_t(D, M_{\infty}, t)$

For samples with sealed edges, such as Asumani's, shown in Figure 4.1, the overall diffusion direction is one-dimensional. The one-dimensional plane wall absorption relation of Equation 2.13 is used to give $M_t = M(D, M_{\infty}, t)$, the total mass of diffusing substance, absorbed by the test sample, after a certain period of time, t.

For samples with unsealed edges, such as Rassmann's, the absorption curve was calculated using the mass absorption-concentration relation in Equation 2.19:

$$\frac{M_t}{M_{\infty}} = 1 - \left(1 - \frac{M_{t,x}}{M_{\infty}}\right) \left(1 - \frac{M_{t,y}}{M_{\infty}}\right) \left(1 - \frac{M_{t,z}}{M_{\infty}}\right)$$

Function to calculate mass absorption infinite sum in Microsoft Excel

In order to calculate mass absorption curves, Equation 2.13 was defined in Microsoft Excel (2010) using a custom Visual Basic for Applications (VBA) function. The code for the function is given in APPENDIX E. The function uses an iterative procedure to add successive terms of the infinite sum until the difference between successive sums is below a specified tolerance (in this case a value of 2^{-52} , corresponding to the limit of the system precision, was used).

The flowchart for the procedure used is shown in Figure 4.4. A generic sum, $Y = \sum_{i=0}^{\infty} X_i$, is used for illustrative purposes. Intermediate values of the sum are given by $Y_k = \sum_{i=0}^{k} X_i$.



Figure 4.4 Flowchart of procedure used to programmatically calculate infinite sum in VBA

Curve fitting

In order to determine diffusion coefficients (D_f and D_c) and saturation mass absorptions ($M_{\infty,c}$) from the experimental data, a least-squares (LS) nonlinear regression method [47] was used to fit the relations in Equations 2.13 (for Asumani's samples with sealed edges) or 2.19 (for Rassmann's samples with unsealed edges) to the experimental mass absorption data. This procedure is outlined below and explained in detail in APPENDIX D.2.

- 1. Initial guesses were made for the values of M_{∞} and D_x , D_y , D_z .
- 2. For each experimental data point, *i*, on the mass uptake-time curve (for example, Figure 4.3), an error was calculated as

$$E_i = M_{exp,i} - M_{curve,i} \tag{4.1}$$

where $M_{exp,i}$ is the measured, experimental value and M_{curve} is the value calculated from Equation 2.13 or 2.19.

3. The sum of the squares of the errors was calculated as

$$SSE = \sum_{i} E_i^2 = \sum_{i} \left(M_{exp,i} - M_{curve,i} \right)^2$$

$$4.2$$

4. Best fit values for M_{∞} and D_x , D_y , D_z were found by using a GRG (Generalised Reduced Gradient) nonlinear algorithm [48], as built in to the Microsoft Excel (2010) solver function, to minimise *SSE* by modifying the initial guess values.

4.2.2 Diffusion properties obtained for thermoset composite samples

The composite diffusion coefficients, D_c , and equilibrium mass absorption, $M_{\infty,c}$, values derived from curve fitting to Rassmann's results are shown in Table 4.1 and Table 4.2. Composite saturated concentrations, $C_{sat,c}$, calculated using $M_{\infty,c}$, the sample density and Equation 2.12 are also shown.

Resin system	Diffusion coefficient, D _c [mm ² /day]				
Fibre v _f	15%	22.5%	30%		
Epoxy	0.052	0.083	0.086		
Polyester	0.100	0.118	0.180		
Vinylester	0.142	0.141	0.138		

Table 4.1Experimentally derived values for thermoset diffusion coefficient, D_c

Resin system	Equilibrium mass absorption,			Saturation	concentration, $C_{sat,c}$	
	<i>M</i> ∞, <i>c</i> [%]			[kg/m ³]		
Fibre v _f	15%	22.5%	30%	15%	22.5%	30%
Ероху	9.61	10.84	13.09	114.7	132.3	163.3
Polyester	6.15	7.54	9.74	78.2	97.3	127.7
Vinylester	3.85	6.06	7.72	45.9	74.0	96.3

Table 4.2Experimentally derived values for thermoset equilibrium mass absorption, $M_{\infty,c}$, and calculated values of saturation concentration, $C_{sat,c}$

4.2.3 Diffusion properties obtained for thermoplastic composite samples

The composite diffusion coefficients, D_c , and equilibrium mass absorption, $M_{\infty,c}$, values derived from curve fitting to Asumani's results are shown in Table 4.3. Composite saturated concentrations, $C_{sat,c}$, were calculated in the same manner as for Rassmann's data. Asumani's samples were presented in terms of the fibre weight fraction, W_f . These were converted to volume fractions using the relation

$$v_f = \frac{W_f \rho_m}{W_f (\rho_m - \rho_f) + \rho_f}$$

$$4.3$$

where typical values of $\rho_m = 900 \text{kg/m}^3$ for polypropylene density and $\rho_f = 1500 \text{kg/m}^3$ for kenaf density were used.

Weight %, W_f	Volume fraction, v_f	<i>M</i> _∞ [%]	$C_{sat,c}$ [kg/m ³]	D _c [mm ² /day]
20%	13.0%	3.64	35.6	0.0033
25%	16.7%	6.21	62.1	0.0073
30%	20.5%	9.57	97.8	0.0396
35%	24.4%	16.89	176.7	0.0706

Table 4.3Diffusion properties, D_c , and $M_{\infty,c}$, for kenaf-polyester thermoplastic samples

4.3 Obtaining fibre and matrix diffusion properties

4.3.1 Determining fibre diffusion coefficient, D_f

The fibre diffusion coefficient, D_f , was estimated from drying and absorption tests carried out by Rassmann [46]. In the drying experiment, he measured the mass loss from a kenaf specimen, originally at room temperature and 45-55% relative humidity (RH), exposed to dry air. The results of this test are shown in Figure 4.5. The absorption experiment measured the absorption of a dried specimen exposed to air at 45-55% RH and room temperature. The absorption measurements are shown in Figure 4.6.

The results of these two test are not suitable for use with the curve fitting method used in the previous section. When compared to the typical absorption curve in Figure 2.5, the drying curve in Figure 4.5 does not have enough points in the initial linear region ($t < t_L$), while the curve in Figure 4.6 contains only points in this region and none beyond it. To predict D_f , the curve fitting method needs data spanning both linear and nonlinear regions.

To overcome this limitation, the saturation mass absorption for a sample in air at 45-55% RH ($M_{\infty,f50}$) was estimated from Figure 4.5. This value was then used with the slope of the data in Figure 4.6 to estimate the fibre diffusion coefficient, D_f . The details of this process are outlined below.

Estimating fibre saturation mass absorption in 45-55% RH air, using drying curve

The fibre sample in Rassmann's drying experiment was in equilibrium with the air at room temperature and 45-55% RH at the start of the experiment and was saturated with moisture. Thus, the net mass lost once the saturated sample has dried is equal to the net mass that would be gained by an initially dry sample that reaches saturation.

Since the drying mass loss is $M_{\infty,d} = \frac{m_{moisture}}{m_{solid} + m_{moisture}}$, the fibre saturation mass absorption at 50% RH, $M_{\infty,f50} = \frac{m_{moisture}}{m_{solid}}$, may be obtained from Figure 4.5 as follows:

$$M_{\infty,f50} = \frac{M_{\infty,d}}{1 - M_{\infty,d}} = 7.22\%$$
4.4

Estimating fibre diffusion coefficient, D_f , from linear slope of absorption curve

The slope of the linear fit to Rassmann's fibre absorption data in Figure 4.6 was used with Equations 2.24 and 2.25 and the sample dimensions to estimate the value of $M_{\infty,f50}\sqrt{D_f}$. Using the previously-obtained value of $M_{\infty,f50} = 7.22\%$ the fibre diffusion coefficient is calculated to be $D_f = 25.3 \text{ mm}^2/\text{day}$.



Figure 4.5 Kenaf fibre mat drying curve for a 3-layered sample in open air oven (after Rassmann [46])



Figure 4.6 Kenaf fibre mat absorption curve for a dry sample exposed to air at 45-55% RH (after Rassmann [46])

4.3.2 Matrix properties and fibre saturation moisture absorption

The literature shows that the saturation concentration for fibre immersed in water is much higher than that exposed to humid air [10]. For this reason, the value of $M_{\infty,f50} = 7.2\%$ was not used for fibre exposed to water. A value of $M_{\infty,f} = 25\%$, based on similar jute fibres, was used instead [13].

Values for resin properties $(D_m \text{ and } M_{\infty,m})$ were taken directly from various sources in the literature. Density values were obtained from supplier data sheets. These values are shown in Table 4.4.

Material	D	M_{∞}	Density	^a C _{sat}	Source
	[mm ² /day]	[%]	[kg/m ³]	[kg/m ³]	
Epoxy (EP)	0.0238	2.41	1139	27.4	[44], [49]
Unsaturated Polyester (UP)	0.00970	3.05	1230	37.5	[50], [51]
Vinylester (VE)	0.165	0.46	1140	5.24	[44], [52]
Polypropylene (PP)	0.1	0.1	900	0.9	[17]
Kenaf mat	^b 25.3	° 25	1500	375	[46], [13]

Table 4.4 Summary of fibre and matrix diffusion property input values

a. Calculated in §4.4.1

b. Calculated in §4.3.1

c. Estimated from value for jute fibre

4.4 Procedure to predict composite diffusion coefficients

The properties in Table 4.4 were used as inputs into the prediction methods to determine the diffusion coefficient, D_c , for various fibre volume fractions, v_f . Specific details of certain prediction methods are outlined below.

4.4.1 Calculating saturation moisture absorption, C_{sat,c}

Where required, the general relation between concentration and moisture absorption in Equation 2.12 ($C = \rho_{solid} M$) was substituted into the definition of $C_{sat,c}$, from Equation 2.30, and the result rearranged to predict the composite saturation moisture concentration from the saturation moisture absorption.

$$C_{sat,c} = (C_{sat,f} - C_{sat,m})v_f + C_{sat,m}$$
$$= (\rho_f M_{\infty,f} - \rho_m M_{\infty,m})v_f + \rho_m M_{\infty,m}$$
4.5

4.4.2 Procedure for Unit cell FE model calculations for the prediction of D_f

Effective diffusion coefficients were first determined for the hexagonal array composite shown in Figure 2.9 for fibre volume fractions ranging from 5% to 80%. The unit cell, with consistent MKS dimensions, was modelled using ANSYS [26] and the relative concentration/wetness fraction approach outlined in §2.2.3. Effective diffusion

coefficients were determined using the volume-averaged directional flux relation of Equation 2.32: $D_{e,y}C_{sat,c} = -\langle F_y \rangle$.

The effective diffusion coefficients for the hexagonal array were used in the random array, shown in Figure 2.10, to determine the composite diffusion coefficient, D_c . A combination of samples was simulated, using β values ranging from 0.1 to 0.6 and fibre volume fractions ranging from 5% to 50%.

The fibre volume fraction of the random array, v_f , was calculated as follows

$$v_f = (1 - \beta^2) v_{f,h}$$
 4.6

where $v_{f,h}$ is the volume fraction of the hexagonal array unit cell.

Representative meshes for the hexagonal array and the random array are shown in Figure 4.7.



Figure 4.7 Hexagonal array and random array meshes

4.4.3 Procedure for Self-consistent model calculations for the prediction of D_f

The diffusion coefficient, D_c , for the self-consistent model was obtained using the iterative approach described by Equations 2.35 and 2.36. This iterative approach was implemented using a custom Microsoft Excel (2010) VBA function with 10 iterations. The code for this function is shown in APPENDIX F.

5 RESULTS AND DISCUSSION

5.1 Thermoset matrix composites



5.1.1 Saturation moisture concentration prediction for thermoset matrix composites

Figure 5.1 Comparison of predicted and experimental thermoset composite equilibrium moisture concentrations, $C_{sat,c}$

Figure 5.1 compares the experimental saturation moisture concentration ($C_{sat,c}$) values calculated from Rassmann's [46] data to prediction lines created using Equation 4.5. The predicted saturation concentration varies significantly from the experimental values: values for epoxy are approximately 21-32% lower than the experimental values, with a root mean square (RMS) error of 25%; those for polyester are 3-13% lower (8.5% RMS); while those for vinylester are 22-40% higher (29% RMS). These error ranges are summarised in Table 5.3.

The discrepancy may be due to a combination of factors, including the input material properties and voids caused by poor fibre-matrix bonding. These will be examined in detail in the next sections.

Effect of input material properties on saturation concentration prediction

In order to assess the effect of input material properties $(\rho_f, M_{\infty,f}, \rho_m, M_{\infty,m})$ on the saturation concentration predictions, a straight line, of the form, y = ax + b, was fitted to the experimental data.

Equation 4.5 $(C_{sat,c} = (C_{sat,f} - C_{sat,m})v_f + C_{sat,m})$ shows that the effective saturation concentration, $C_{sat,c}$, is a linear function of the fibre volume fraction, v_f , so the intercept

of the fitted line, *b*, should give an estimate of the actual saturation concentration of the matrix material, $C_{sat,m}$, while the slope, *a*, should estimate the difference between the actual saturation concentrations of the fibre and matrix ($C_{sat,f}$, $C_{sat,m}$).

These estimated values are compared to the input values from Table 4.4. The results of this comparison are shown in Table 5.1. Using these values, the overall predictions improved, as shown in Table 5.3.

Resin system	Data from curve	fit	Deviation from input data		
	C _{sat,f} [kg/m ³] C _{sat,m} [kg/m ³]		$\Delta C_{sat,f}$	$\Delta C_{sat,m}$	
Epoxy	387.7	63.9	10.0%	132.8%	
Polyester	357.0	26.8	1.3%	80.3%	
Vinylester	332.4	-3.5	-5.7%	-133.0%	

Table 5.1Deviation of input fibre and thermoset matrix saturation concentration valuesfrom values obtained from a linear fit to experimental data.

The data shows that the value for the fibre saturation concentration, $C_{sat,f}$, chosen for the analysis is close to the values obtained from the curve fit (between -6% and 10%) and indicates that the value chosen from the literature is likely to be close to the true value for the fibre.

The linear fit values for the matrix saturation concentration, $C_{sat,m}$, are higher than the literature values used for epoxy and polyester, indicating that the values obtained from the literature may be lower than actual values for the specific resins used. The negative value for the vinylester composite would not be possible physically and may indicate another cause for the lower values. Rassmann [46] noted some difficulties while manufacturing the vinylester samples, but implications of this have not been investigated further here.

The resin manufacturers do not include values for the saturation concentration, $C_{sat,m}$, in their material datasheets, while the values in the literature may have been obtained from resins with different compositions, catalysts and curing conditions.

Ideally, pure resin samples should have been created from the same batch of resin used to manufacture the composite samples and then cured under the same conditions, before being used in absorption tests to get specific resin properties.

Such tests were, indeed, performed by Rassmann [46] but they did not progress beyond the initial linear region of the absorption process, rendering them unsuitable for predicting all resin properties ($C_{sat,m}$, D_m).

Effect of moisture voids on saturation concentration prediction

Although Rassmann [46] did not note the presence of visible voids in his test samples, it is possible that small voids, perhaps caused by poor fibre-matrix adhesion, may have escaped notice and may still have had some effect on the saturation concentration values. These voids would generally lead to an under-prediction of the concentration, as was noted in the literature survey, §2.6.1. Such an under-prediction was observed for epoxy and polyester samples, but not for vinylester.

Equation 2.30 can be modified to account for the voids, giving the saturation concentration as a function of the fibre and void volume fractions (this derivation is shown in APPENDIX A.3):

$$C_{sat,c} = C_{sat,f} v_f + C_{sat,m} (1 - v_f - v_v) + \rho_w v_v$$

= $(C_{sat,f} - C_{sat,m}) v_f + [(\rho_w - C_{sat,m}) v_v + C_{sat,m}]$ 5.1

where ρ_w is the moisture density.

To analyse the effect of voids, it was assumed that the fibre and matrix input material properties were correct. A straight line (y = ax + b) was, again, fitted to the experimental data points in Figure 5.1. The void fraction was then calculated by comparing the intercept, *b*, to the second term in Equation 5.1.

The void fractions estimated in this way are shown in Table 5.2. Using these values, the overall predictions improved, as shown in Table 5.3.

Resin system	Properties from	m input data	
	C _{sat,f} [kg/m ³]	C _{sat,m} [kg/m ³]	Void fraction, v_v
Epoxy	375	27.4	0.038
Polyester	375	37.5	0.011
Vinylester	375	5.24	-0.016

 Table 5.2
 Void volume fraction, estimated from experimental saturated concentration

Void fractions of 1-4% would produce better predictions for the epoxy and polyester composite samples, though a value as high as 4% would likely have been noted by Rassmann. Ideally, a microscopic analysis of the test samples should have been performed to check for voids invisible to the naked eye and to estimate the void fraction.

			^a Original properties
	^a Original properties	^b Modified properties	with void fraction
Epoxy	25% RMS	2.3% RMS	3.4% RMS
Polyester	8.5% RMS	2.6% RMS	4.5% RMS
Vinylester	29% RMS	1.9% RMS	4.8% RMS

Table 5.3Summary of saturated concentration prediction error using original properties,
modified properties and original properties with void fraction

a. Properties from Table 4.4

b. Properties from Table 5.1.

5.1.2 Diffusion coefficient prediction for thermoset matrix composites

The diffusion coefficients, D_c , predicted by the thermal resistance analogy (Equation 2.28), three- and four-phase models (Equations 2.33 and 2.37) and the self-consistent model (Equations 2.35 and 2.36) are shown in Figure 5.2, together with the experimental values calculated from Rassmann's [46] results. All results are normalised with the matrix diffusion coefficient, D_m . The predicted normalised diffusion coefficients (D_c/D_m) are almost identical for the three resins, so only one curve is shown for each model.



Figure 5.2 Comparison of predicted and experimental thermoset composite diffusion coefficients

Figure 5.3 shows the composite diffusion coefficients predicted by the unit cell FE model with $\beta = 0$. Experimental values are not shown as they are significantly higher than the predicted values.



Figure 5.3 Thermoset composite diffusion coefficients, D_c , predicted by unit cell FE model with $\beta = 0$

The deviations of the various prediction models from the experimental results are summarised in Table 5.4. It is clear that all the prediction methods substantially underpredict the composite diffusion coefficient, D_c . As was suggested in §2.6 in the literature survey, this could be related to the conflict between assumptions made by the prediction methods and the actual state of the composite, including the fibre arrangement and moisture and voids paths due to poor fibre-matrix bonding. In addition there may have been discrepancies in the material properties, and possible errors in the experimental data. Each of these are discussed in the following subsections.

		Deviation from input data			
Prediction model	Resin system	Max.	Min.	RMS	
Thermal resistance analogy	Ероху	59% lower	43% lower	53%	
	Polyester	43% lower	23% lower	32%	
	Vinylester	53% lower	35% lower	45%	
Three-phase model	Epoxy	55% lower	38% lower	47%	
	Polyester	36% lower	16% lower	25%	
	Vinylester	49% lower	27% lower	39%	
Four-phase model ($v_v =$	Epoxy	54% lower	36% lower	46%	
1%)	Polyester	35% lower	15% lower	24%	
	Vinylester	47% lower	26% lower	38%	
Self-consistent model	Epoxy	52% lower	36% lower	44%	
	Polyester	29% lower	13% lower	20%	
	Vinylester	47% lower	20% lower	36%	
Unit cell FE model	Epoxy	89% lower	78% lower	85%	
	Polyester	92% lower	82% lower	87%	
	Vinylester	93% lower	91% lower	93%	

Table 5.4Summary of deviation of predicted thermoset composite diffusion coefficients
from experimental values for five prediction models

Errors in predictions of D_c due to fibre arrangement

As noted in §2.6, all of the unit cell methods assume that the fibres are unidirectional and are oriented perpendicular to the diffusion plane. As shown in the unit cell model in Figure 5.4a, this implies that the permeable fibres are not in direct contact with the diffusing substance at the edges of the cell, but are surrounded by a uniform layer of less permeable matrix or homogeneous medium. This also implies that there is no direct contact between adjacent fibres (all diffusion passes through an intermediate layer of matrix).



Figure 5.4 Representation of fibre orientations and moisture paths in typical unit cell model and actual water absorption specimen

The fibres used to manufacture the test samples were in the form of needle-punched mats and did not have uniform fibre orientation. A representation of the fibre orientation of the mat is shown in Figure 5.4b. The majority of fibres have a general orientation in the direction of the roll, with a smaller number oriented across the roll direction. The fibre orientation through the thickness is also not uniform, due to the needle punch manufacturing method, as illustrated in Figure 5.5.



Figure 5.5 Section through needle-punched mat (after [53])

The non-uniform fibre arrangement implies that some fibres come into direct contact with the surrounding medium at the sample edges or else the thickness of the matrix surrounding them is reduced in places. Secondly, the woven mat of the experimental samples brings some fibres into contact, allowing direct diffusion between these fibres. As a result, the amount of moisture that is able to diffuse directly along the fibres is much greater, causing higher-than-predicted experimental composite diffusion coefficients. The FE unit cell methods attempted to address the problem of non-uniform fibre spacing by introducing the β coefficient. Figure 5.6 shows the effect of increasing values of β for epoxy composites. It is clear that increasing β does not cause a large enough increase in the composite diffusion coefficient, over the volume fraction range of interest (15% to 30%), to significantly improve the prediction. This is understandable, since the model is still limited by the assumption that all fibres lie perpendicular to the diffusion plane.



Figure 5.6 Effect of increasing β in the unit cell FE model to account for non-uniform fibre arrangements

Errors in predictions of D_c due to moisture voids

Improper fibre-matrix bonding and the presence of voids in the composite would increase both the number of moisture paths and the apparent diffusion coefficient of experimental samples. The four-phase model from Gueribiz et al. [42] attempts to account for this by including a moisture-filled void around the fibre. The effect of this void fraction, v_v , is shown in Figure 5.7. Although a value of $v_v = 10\%$ does improve the prediction, it is significantly higher than the 1%-4% values discussed in §5.1.1 and would lead to visible flaws in the composite which Rassmann did not observe in his samples [46]. In addition, such high void fractions would significantly increase the amounts of fluid transported by flow and percolation, rather than diffusion, and would lead to significant non-Fickian behaviour. This was not observed in Rassmann's data.



Figure 5.7 Effect of increasing v_v in the four-phase model, compared to experimental results for polyester

Errors in predictions of D_c due to input material properties

The variation in input material properties for the resins, mentioned in §5.1.1, may account for the predicted composite diffusion coefficients, D_c , being lower than the experimental values. This would be the case if the actual matrix diffusion coefficients, D_m , were higher than the values used in this work. The diffusion predictions are, however, dominated by the fibre diffusion coefficient, D_f , which is several orders of magnitude higher than D_m . It is thus unlikely that errors in the prediction of D_m can entirely account for the underprediction of D_c .

Errors in the prediction of the fibre diffusion coefficient, D_f , would have a larger impact on the under-predicted composite diffusion coefficients than errors in D_m . In order for this to be the case, the actual fibre diffusion coefficients would have to be higher than the value of $D_f = 25 \text{ mm}^2/\text{day}$ that was used. Figure 2.7 shows that the peak diffusion coefficient, D_f , for a natural fibre typically occurs around 50% relative humidity, corresponding to the conditions present for Rassmann's sorption test on the fibre mat [46]. This suggests that the actual fibre diffusion coefficient may, rather, be lower than the value used and would indicate that errors in fibre diffusion coefficient prediction are not responsible for the under-prediction.

Errors in experimental measurements of D_c

There are two potential sources of error in the experimental validation data. The first is that the tests performed by Rassmann were not carried out to equilibrium, but were instead terminated after four weeks [46]. As result, the majority of the absorption data points lie in the linear region of the absorption curve and only the last two to three begin to deviate from this linear behaviour. This is especially noticeable in the 15% volume fraction samples, particularly those for epoxy. As noted in §4.2.1, discussing the measurement of fibre properties, the curve fitting method needs sufficient data points in both the linear and nonlinear regions to provide adequate estimates of both the diffusion coefficients and saturation moisture absorption, so the experimental values for D_c and $M_{\infty,f}$ obtained here may not be accurate.

The second source of error is that the samples used by Rassmann did not have sealed edges and were able to absorb moisture on all six sides. Although the length/thickness ratio of the samples was above 10, the long axes of the samples were aligned with the general fibre direction (as illustrated in Figure 5.4b), leading to increased absorption in these directions. The assumption of 1D flow into the sample in the thickness direction is, thus, not valid. An attempt was made to account for this by performing the curve fitting using the 3D form of the Fickian mass absorption equation. This, however, introduces four extra variables to the curve fitting procedure and compounds the problems outlined in the previous paragraph.

Finally, the experiments were only performed for three volume fractions, increasing the effects of any extraneous values.

The experimental data should be improved by performing the absorption experiments on samples with sealed edges to ensure 1D absorption. The experiments should, ideally, be carried out until they reach equilibrium. Sealing the edges will, however, significantly reduce the rate of moisture absorption and increase the experiment time. It may not be feasible to test until equilibrium is reached. In this case, the experiments should be run long enough to generate a number of data points outside the linear region of the absorption curve. The number of volume fractions tested should also be increased, as is the case with the Asumani's [45] polypropylene test data.

5.1.3 Formulating the bidirectional fibre model to predict thermoset composite diffusion coefficient

In order to account for the non-uniform fibre arrangement, discussed in §5.1.2, Shen and Springer's [31] resistance analogy was modified to produce a new prediction relation, the

bidirectional fibre prediction method, incorporating fibres lying parallel to the direction of moisture diffusion. This method attempts to overcome some of the limitations discussed in §2.6 by accounting for fibres that lie parallel to the diffusion plane and allowing the model to accommodate situations where the matrix is impermeable.

The model is based on the unit cell shown in Figure 5.8. The cell has unit depth with width and height 2a and 2b. The cell is symmetrical about the centreline, the parallel fibres are represented by two strips of width, t, and the perpendicular fibres by a circle of radius, r. It is assumed that flow only occurs in the parallel direction.



Figure 5.8 Modified unit cell for bidirectional fibre method

The full derivation of the bidirectional fibre method is given in APPENDIX E and the resulting diffusion coefficient, in the principal diffusion direction, is given by Equation 5.2:

$$\frac{D_c}{D_m} = 1 - v_f F_D \left(\frac{B_D}{B_D + 2}\right) - 2\sqrt{\frac{v_f (1 - F_D)}{\pi}} + \frac{1}{B_D} \left[\pi - \frac{4}{\sqrt{1 - B_D^2 (v_f (1 - F_D)/\pi)}} \left(\operatorname{atan} \frac{\sqrt{1 - (B_D^2 v_f (1 - F_D)/\pi)}}{1 + B_D \sqrt{v_f (1 - F_D)/\pi}} \right) \right] 5.2$$

where $B_D = 2\left(\frac{D_m}{D_f} - 1\right)$ and $F_D = \frac{v_{f\parallel}}{v_f}$.

The method introduces a fibre direction coefficient, F_D . For a purely bidirectional composite with continuous fibres extending completely through the composite, F_D may be interpreted as the volumetric fraction of fibres that are lying parallel to the overall diffusion direction. For a multidirectional composite with non-continuous fibres of general orientation, F_D would be related to the specific fibre arrangement of the material used to manufacture that composite and would be determined empirically. In this case,

materials with a similar fibre arrangements (e.g. woven vs. needle punched mat vs. chopped strand mat etc.) should have a similar value of F_D .

To test the similarity of F_D across different composites with similar fibre structure, a value for F_D was obtained for the epoxy-kenaf composite and was used as an input in Equation 5.2 to predict the composite diffusion coefficient, D_c , for the polyester- and vinylester-kenaf composites. The predictions were then compared to the measured values for these two composites. This is outlined in detail in the following sections.

Estimating F_D for needle-punched kenaf mat

To determine a value of F_D , Equation 5.2 was fitted to the experimental data from Table 4.1 for the epoxy-kenaf composite. The curve fitting procedure described in §4.2.1 was used with F_D as the input variable and $E_i = D_{c,exp,i} - D_{c,curve,i}$ used as the error function, where $D_{c,exp}$ is the experimental value for D_c at some volume fraction and $D_{c,curve}$ is the corresponding value calculated using Equation 5.2.

This produced a fibre direction coefficient of $F_D = 0.0069$ for the needle-punched kenaf mat. The RMS error for the prediction for the epoxy-kenaf composite was reduced to 9%, with the maximum error improving to 12% below the experimental values. This improved prediction is shown in Figure 5.9.

Using the estimated value of F_D to predict diffusion coefficients for other resin systems with needle-punched kenaf mat

All of the samples in Table 4.1 were made from the same needle-punched kenaf mat. The F_D value, which is based on the fibre arrangement, should thus be the same for each sample. Figure 5.9 compares the experimental data for the polyester- and vinylester-kenaf composites to the diffusion coefficients predicted by Equation 5.2, using the value of $F_D = 0.0069$ that was obtained for the epoxy samples.

The RMS error in the predictions is reduced compared to those in Table 5.4, with the value for UP now at 9.4%, while that for VE is 22%. The maximum deviations are 14% and 35% below for UP and VE respectively.



Figure 5.9 Comparison of experimental data with bidirectional fibre model predictions for $F_D = 0.0069$

Sources of error for the bidirectional fibre model predictions

Although the bidirectional fibre model improves the composite diffusion coefficient prediction, there is still some variation, particularly for the vinylester composite. In addition to the limitations of the experimental data, discussed in §5.1.2, there are two other potential causes for the variation.

First, the bidirectional fibre model does not account for the discontinuous moisture concentration that can occur at the interface between two materials. It may need to be modified to incorporate the relative, rather than absolute, concentration field. This modification was not performed in the current work.

Second, the bidirectional fibre model does not specifically account for fibres that may loop over each other or double back before reaching the other end of the sample. The empirical direction coefficient, F_D , is intended to account for this, but the nine experimental data points (three resin systems at three volume fractions) are not sufficient to confirm this. Further testing, particularly covering a larger number of fibre volume fractions, is required to determine whether the direction coefficient is sufficient or whether a model that specifically accounts for varying moisture paths, such as the percolation model of Wang et al. [54] would be more applicable.
5.2 Thermoplastic matrix composites



5.2.1 Saturation moisture concentration prediction for thermoplastic matrix composites

Figure 5.10 Comparison of predicted and experimental thermoplastic composite equilibrium moisture concentrations, $C_{sat,c}$

Figure 5.10 compares the experimental saturation moisture concentration ($C_{sat,c}$) values calculated from Asumani's [45] data for polypropylene-kenaf composites to prediction lines created using Equation 4.5. The predicted saturation concentration varies significantly from the experimental values: from 31% higher to 51% lower as the volume fraction increases.

As with the thermoset composites, the discrepancy may be due to a combination of factors, including the input material properties and moisture paths caused by poor fibrematrix bonding. These will be examined in detail in the next sections.

Effect of input material properties on saturation concentration prediction

The literature indicates that polypropylene is highly hydrophobic and does not absorb significant amounts of water [17,45]. The absorption curves given there do not reach equilibrium and the actual values of moisture absorbed are extremely low. Law and Mohd Ishak's [17] data shows only a 0.1% increase in sample mass after a week, while Asumani [45] found no measurable increase in sample mass after several months of absorption. This near-impermeable matrix may lead to regions that are inaccessible to moisture, as discussed in §2.6, and may explain the under-prediction of the saturation concentration at lower volume fractions.

Using the same linear fit method, described in §5.1.1 for the thermoset saturation concentration, to fit Equation 4.5 to the polypropylene v_f - $C_{sat,c}$ curve in Figure 5.10 gives a best fit relation of $C_{sat,c} = 1217v_f - 134$. This curve predicts that at a fibre volume fraction, $v_f = 11\%$, the composite saturation concentration, $C_{sat,c}$ will be zero. This implies that there may be some critical fibre volume fraction below which the polypropylene composite will absorb negligible amounts of moisture. This will be examined in more detail in §5.2.3 when the polypropylene diffusion coefficient is discussed.

Effect of moisture voids on saturation concentration prediction

In §5.1.1, it was observed that accounting for voids and poor fibre-matrix bonding would shift the saturation concentration curve upwards by a certain amount, but would not affect its slope. The predicted slope $(C_{sat,f} - C_m = 352 \text{ kg/m}^3)$ for the polypropylene-kenaf saturation concentration, $C_{sat,c}$ is four times lower than the actual slope (1217 kg/m³) fitted through the experimental data. This indicates that the presence of voids or poor fibre-matrix bonding is unlikely to be the principal reason for the observed deviation.

5.2.2 Diffusion coefficient predictions for thermoplastic matrix composites

The diffusion coefficients, D_c , predicted by the thermal resistance analogy (Equation 2.28), three- and four-phase models (Equations 2.33 and 2.37) and the self-consistent model (Equations 2.35 and 2.36) are shown in Figure 5.11 together with the experimental values calculated from Asumani's [45] results. All results are normalised with the matrix diffusion coefficient, D_m .



Figure 5.11 Comparison of predicted and experimental polypropylene composite diffusion coefficients

Figure 5.12 shows the composite diffusion coefficients predicted by the unit cell FE model with $\beta = 0$. Only one experimental value is shown, as the rest are significantly higher than the predicted values.



Figure 5.12 Polypropylene composite diffusion coefficients, D_c , predicted by unit cell FE model with $\beta = 0$

It is clear that most of the prediction methods substantially over-predict the composite diffusion coefficient, D_c , at lower fibre volume fractions (<20%) and under-predict it at higher volume fractions. As was observed for the saturation concentrations, $C_{sat,c}$, in §5.2.1, there appears to be a cut-off volume fraction, around 11%, below which no diffusion takes place.

In §5.1, it was suggested that the reason for the thermoset results deviating from the predictions could be due to the fibre structure, the presence of moisture paths, error in the material properties, or problems with the validation data. These same explanations are now examined for the polypropylene samples.

Errors in predictions of D_c due to fibre arrangement

The polypropylene samples were produced by compressing the fibre mat and plastic pellets in a heated mould. This would flatten the mat to some extent and bring the fibres that lie across the sample thickness closer to a unidirectional arrangement, which could increase the diffusion in a sample with unsealed edges, where one of the principal diffusion directions would lie parallel to the fibres. The edges of the polypropylene samples are, however, sealed, and these compressed fibres still remain perpendicular to the overall diffusion direction, so this is unlikely to be a cause of the rapid change in diffusion coefficient observed for the experimental results.

Although the bidirectional fibre model was formulated to account for differing fibre arrangements, it is not able to account for the steep slope of the polypropylene data, even with high values of the direction coefficient, F_D . The model does not provide an adequate description of the polypropylene-kenaf composite behaviour and there may be other causes, other than the fibre orientation, for the observed composite diffusion behaviour.

Errors in predictions of D_c due to moisture voids

As discussed in §5.1.2 for thermoset materials, the void fraction in the four-phase model would need to be raised to an unrealistic level in order to account for the highest values of the experimental diffusion coefficients, D_c , that were observed for the polypropylene composite. In addition, the increase in diffusion coefficient with increasing void fraction, seen in Figure 5.7, does not adequately explain the steep slope of the experimental data for polypropylene. The compression moulding technique used to manufacture the polypropylene would also reduce the size of voids in the composite.

Errors in predictions of D_c due to input material properties

Polypropylene experiences extremely low moisture absorption, to the point where it would be valid to treat it as an impermeable material [17,45]. The prediction relations used were generally formulated to account for cases where the fibres were impermeable, rather than the matrix. These methods produce singularities when used with impermeable matrix material and may produce anomalous predictions for near-impermeable materials, as was noted in §2.6. The impermeable nature of polypropylene renders the current prediction relations invalid and points to the requirement for a different method to predict the diffusion properties. One such possible approach is discussed in §5.2.3.

Errors in experimental measurements of D_c

The polypropylene samples were produced with sealed edges, and so give a reasonable representation of 1D diffusion through the sample thickness. In addition, the absorption experiments were run to equilibrium. This allowed a good prediction of the diffusion coefficients, D_c , and saturation concentration, $C_{sat,c}$, either by inspection of the linear gradient and final values, or by using a curve fit with the 1D mass absorption relation. It is thus unlikely that errors in the validation data are a major cause of the differences between experimental predicted values.

5.2.3 Percolation theory to predict polypropylene matrix composite behaviour

The apparent existence of a fibre volume fraction below which moisture absorption may not occur, observed in Figure 5.10 and Figure 5.11, indicates that absorption may not be a

pure diffusion process. Wang et al. [54] began to address the behaviour of natural fibre composites with impermeable matrices by introducing concepts from percolation theory to describe absorption in these materials.

Their approach represents the composite as a square lattice where each individual cell is randomly assigned either matrix or fibre properties. The probability that a particular cell will be fibre is equal to the fibre volume fraction. Lattices for low and high fibre contents are shown in Figure 5.13 (grey squares indicate fibres). At low fibre contents, the fibres exist individually or in isolated clusters. If the top surface is exposed to moisture and the side surfaces are sealed, there is no available path for moisture to reach the bottom surface, resulting in zero observed diffusion. In addition, isolated clusters will not contribute to the apparent saturation concentration, even if diffusion is occurring through other parts of the composite. At high fibre contents, large clusters form and there are fewer isolated fibres. There are many paths for moisture to transfer from the top to bottom surfaces.



Figure 5.13 Fibre distributions in plastic at different fibre contents [54]

Wang et al. [54] suggested that, as the fibre content increases, the isolated clusters grow until they reach a fibre content where a cluster is formed that spans from the top to bottom surfaces. They named this spanning cluster the 'infinite cluster' and called the fibre content at which it was formed the 'percolation threshold' or 'critical fibre content'. Figure 5.14 shows the flow passages present once the infinite cluster has formed. Wang et al. described three fibre types connected to the flow passage. Those labelled 'F' form flow passages and contribute directly to the moisture conductivity (analogous to diffusivity). Those labelled 'e' are dangling ends of the infinite cluster. They absorb moisture, increasing the saturation concentration, but do not contribute to the moisture conduction. Finally, those labelled '1' form loops within the infinite cluster, but do not contribute to the conductivity. Like the 'e' fibres, they also contribute to the total absorption. The ratio of fibres lying in the infinite cluster, or lying on a surface in contact with external moisture, to the total number of fibres, was named the 'accessible fibre ratio'.



Figure 5.14 Flow passages in lattice with different fibre contents [54]

Wang et al. [54] performed absorption tests on rice husk-HDPE composites. They concluded that, at high fibre volume fractions (65%) and high accessible fibre ratios (0.91), diffusion was the dominant absorption mechanism, while at low volume fractions close to and below the percolation threshold, percolation was the dominant mechanism. They estimated that the percolation threshold was around 45% fibre volume fraction. Their work did not directly attempt to estimate the diffusion properties (D_c , $C_{sat,c}$).

The percolation mechanism described by Wang et al. [54] may provide a suitable explanation for the observed absorption behaviour of Asumani's [45] polypropylene-kenaf samples. The extrapolated point, around 11% volume fraction, in the experimental data where moisture absorption ceases, would correspond to Wang et al.'s [54] percolation threshold.

Using fibre mat, rather than individual rice husks, for the supporting fibre should increase the likelihood of moisture passages forming. The individual fibres in the mat act as 'pre-formed' moisture paths. This would explain why the observed percolation thresholds (the extrapolated points, at 10%-20% volume fraction, in the experimental data) are lower than the 45% value observed by Wang et al. [54].

No attempt has been made in the present work to implement percolation theory, but it presents a potential avenue for future work.

6 CONCLUSION AND RECOMMENDATIONS

6.1 Conclusions

6.1.1 Thermoset matrix composite results

Saturation concentration predictions for thermoset matrix composites

- 1.) The composite saturation concentration, $C_{sat,c}$, values for the epoxy-, polyesterand vinylester-kenaf thermoset composites were not accurately predicted.
- 2.) The thermoset saturation concentration deviation may be due to incorrect input material properties $(D_m, C_{sat,m})$ for the matrix or the presence of voids in the composite.
- 3.) Modifying the composite saturation concentration prediction method from the literature to account for voids in the matrix, and using a void fraction of 3.8% for the epoxy samples and 1.1% for the polyester samples, improved the experimental predictions.

Diffusion coefficient predictions for thermoset matrix composites

- 1.) The five diffusion coefficient prediction methods that were analysed produced results that deviated significantly from the experimental data.
- 2.) The resistance analogy, three- and four-phase models and self-consistent models produced predicted values of D_c that were lower than the experimental values with RMS errors ranging from 20% to 53%, while the unit cell FE model's predictions were lower with an RMS error of 93%.
- 3.) The major deviation in thermoset diffusion coefficient prediction may be due to assumptions about the fibre structure made by the prediction methods.
- 4.) The bidirectional fibre model was created to account for non-unidirectional fibres and non-uniform fibre layout. An empirical fibre direction coefficient, F_D , was included to account for the fibre arrangements.
- 5.) Materials with similar fibre structures, e.g. needle-punched kenaf mat, should have similar values for F_D .
- 6.) Fitting the bidirectional fibre model to the epoxy-kenaf experimental diffusion coefficients, D_c , determined that a value of $F_D = 0.0069$ was representative of needle-punched kenaf mat. This value reduced the RMS error in predicting epoxy-kenaf diffusion coefficient to 9%.
- 7.) The same value of F_D , applied to the polyester and vinylester samples, brought their RMS errors down to 9% and 22%, respectively.

6.1.2 Thermoplastic polypropylene matrix composite results

Saturation concentration predictions for polypropylene matrix composites

- The composite saturation concentration values for the thermoplastic polypropylene-kenaf composite were not accurately predicted. The slope of the experimental data suggested that there may be some fibre volume fraction (in this case 11%) below which no absorption takes place.
- 2.) The inaccurate polypropylene saturation concentration predictions may be explained by the near-impermeable nature of the matrix. Under these conditions, the dominant absorption mechanism may be percolation rather than diffusion and there may be regions of the composite that are isolated from moisture.

Diffusion coefficient predictions for polypropylene matrix composites

- 1.) The polypropylene-kenaf experimental data did not show any match to the predicted results from any of the models. The experimental data slope suggested that there may be some fibre volume fraction (in this case 11%) below which no absorption takes place.
- 2.) The moisture absorption of the polypropylene may be a percolation process. Fibres completely surrounded by matrix, not in contact with a surface exposed to moisture and not part of an infinite cluster, will absorb no moisture. Below the percolation threshold (likely around 11% fibre volume fraction) little to no absorption will occur, due to the absence of continuous moisture passages.

6.2 Recommendations

- 1.) Matrix material property $(D_m, C_{sat,m})$ data should be improved by using values obtained from sorption tests carried out on resin samples manufactured from the same resin batch, and under the same curing conditions, as the composite samples. The tests should capture a number of data points outside the linear region of the absorption-time^{1/2} curve and preferably run until equilibrium is reached.
- 2.) The thermoset composite absorption experimental data should be improved by testing samples with sealed edges and at more than three fibre volume fractions per matrix material. These should last long enough to adequately capture or predict the equilibrium behaviour.
- 3.) Further work should be performed to determine whether models based on percolation theory and Wang et al.'s [54] work can adequately explain the behaviour of impermeable matrix polypropylene-kenaf composite.

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APPENDIX A DERIVATION OF ABSORPTION AND RELATIONS

A.1 Derivation of Equation 2.13 for net mass absorbed over time

The concentration of diffusing substance at a particular location may be written in differential form as:

$$C = \frac{dm_{moisture}}{dV}$$
A.1

The total amount of diffusing substance in a given volume is then obtained by integration and is given as:

$$m_{moisture} = \int_{V} C dV$$
 A.2

For the case of a one dimensional geometry of cross sectional area, A, and depth, l this becomes:

$$m_{moisture} = A \int_0^l C dx$$
 A.3

Equation A.3 and Equation 2.11 are combined and rearranged as shown below:

$$\frac{m_{moisture}}{A} = \int_{0}^{l} C(x,t) dx$$

$$= \int_{0}^{l} \left[C_{s} - \frac{4}{\pi} (C_{s} - C_{0}) \sum_{n=0}^{\infty} \frac{1}{2n+1} \sin \frac{(2n+1)\pi x}{l} \exp\{-(2n+1)^{2} \pi^{2} t^{*}\} \right] dx$$

$$= C_{s} l - \frac{4}{\pi} (C_{s} - C_{0}) \int_{0}^{l} \left[\sum_{n=0}^{\infty} \frac{1}{2n+1} \sin \frac{(2n+1)\pi x}{l} \exp\{-(2n+1)^{2} \pi^{2} t^{*}\} \right] dx$$
A.4

Using the sum rule for integration this can be rearranged into the infinite sum of a series of integrals as:

$$\frac{m_{moisture}}{A} = C_s l - \frac{4}{\pi} (C_s - C_0) \sum_{n=0}^{\infty} \int_0^l \left[\frac{1}{2n+1} \sin \frac{(2n+1)\pi x}{l} \exp\{-(2n+1)^2 \pi^2 t^*\} \right] dx$$
 A.5

Which can be rearranged using basic integration rules to give:

$$\frac{m_{moisture}}{A} = C_s l - \frac{4}{\pi} (C_s - C_0) \sum_{n=0}^{\infty} \frac{\exp\{-(2n+1)^2 \pi^2 t^*\}}{2n+1} \int_0^l \sin\frac{(2n+1)\pi x}{l} dx$$
$$= C_s l - \frac{4}{\pi} (C_s$$
$$- C_0) \sum_{n=0}^{\infty} \frac{\exp\{-(2n+1)^2 \pi^2 t^*\}}{2n+1} \left[-\frac{l}{(2n+1)\pi} \cos\frac{(2n+1)\pi x}{l} \right]_0^l$$
$$= C_s l - \frac{4l}{\pi^2} (C_s - C_0) \sum_{n=0}^{\infty} \frac{\exp\{-(2n+1)^2 \pi^2 t^*\}}{(2n+1)^2} \left[-\cos(2n+1)\pi + 1 \right]$$
A.6

 $\cos(2n+1)\pi = -1$ for all integer values of *n*, so the equation becomes:

$$\frac{m_{moisture}}{A} = C_s l - \frac{8l}{\pi^2} (C_s - C_0) \sum_{n=0}^{\infty} \frac{\exp\{-(2n+1)^2 \pi^2 t^*\}}{(2n+1)^2}$$
A.7

Setting t = 0 in the Equation A.7 gives the initial mass of moisture, $m_{moisture,0} = C_0 Al$. The net mass of diffusing substance that has crossed the boundary after a certain time is then:

$$\begin{split} m_{moisture} - m_{moisture,0} &= A \left(C_s l - C_0 l - \frac{8l}{\pi^2} (C_s - C_0) \sum_{n=0}^{\infty} \frac{\exp\{-(2n+1)^2 \pi^2 t^*\}}{(2n+1)^2} \right) \\ &= A l (C_s - C_0) \left(1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{\exp\{-(2n+1)^2 \pi^2 t^*\}}{(2n+1)^2} \right) \end{split}$$

$$A.8$$

Dividing through by the solid mass, $m_{solid} = \rho_{solid}Al$, gives:

$$M = \frac{m_{moisture} - m_{moisture,0}}{m_{solid}} = \frac{1}{\rho_{solid}} (C_s - C_0) \left(1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{\exp\{-(2n+1)^2 \pi^2 t^*\}}{(2n+1)^2} \right)$$
A.9

where M is the net amount of substance absorbed, relative to the dry mass.

Finally, the saturation mass absorption, M_{∞} , can be included to give Equation 2.13 as shown below.

$$M_t = M_{\infty} \left[1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\{-(2n+1)^2 \pi^2 t^*\} \right]$$
 A.10

where $M_{\infty} = \lim_{t \to \infty} M_t = (C_s - C_0) / \rho_{solid}$

A.2 Derivation of Equation 2.19 for mass absorption in a parallelepiped.

As described in APPENDIX A.1 the mass of diffusing substance in a body at a specific time may be obtained from the volume integral of concentration field at that time. For the case of a three-dimensional parallelepiped of dimensions l_x , l_y and l_z , the volume integral in Equation A.2 becomes:

$$m_{moisture} = \int_0^{l_z} \int_0^{l_y} \int_0^{l_x} C(x, y, z, t) dx \, dy \, dz$$
 A.11

Equation 2.18 is modified into a similar form to Equation 2.11 by shifting the axes, using the substitutions $x_1 = x - l_x/2$, $x_2 = y - l_y/2$ and $x_3 = z - l_z/2$, together with $l_1 = l_x$, $l_2 = l_y$ and $l_3 = l_z$. This gives:

$$C(x, y, z, t) = C_s \left[1 - \left(\frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)} \cos \frac{(2n+1)\pi \left(x - \frac{l_x}{2}\right)}{l_x} \exp \left\{ - \left(\frac{(2n+1)\pi}{l_x} \right)^2 D_x t \right\} \right) \right]$$

$$\times \left(\frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)} \cos \frac{(2n+1)\pi \left(y - \frac{l_y}{2}\right)}{l_y} \exp \left\{ - \left(\frac{(2n+1)\pi}{l_y} \right)^2 D_y t \right\} \right) \right]$$

$$\times \left(\frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)} \cos \frac{(2n+1)\pi (z - \frac{l_z}{2})}{l_z} \exp \left\{ - \left(\frac{(2n+1)\pi}{l_z} \right)^2 D_z t \right\} \right) \right]$$

Using standard phase shifts and recognising that n is an integer, the cosine functions can then be converted to sine functions:

$$\cos\frac{(2n+1)\pi\left(x_i-\frac{l_i}{2}\right)}{l_i} = \cos\left[(2n+1)\pi\left(\frac{x_i}{l_i}\right) - (2n+1)\frac{\pi}{2}\right]$$
$$= \cos\left[-(2n+1)\pi\left(\frac{x_i}{l_i}\right) + n\pi + \frac{\pi}{2}\right]$$
$$= (-1)^n \sin\frac{(2n+1)\pi x_i}{l_i}, n \in \mathbb{Z}$$

Replacing the cosine functions and inserting the revised concentration relation into Equation A.11, the mass of substance in the sample is:

$$\begin{split} m_{moisture} &= \int_{0}^{l_{z}} \int_{0}^{l_{y}} \int_{0}^{l_{x}} C_{s} \left[1 - \left(\frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^{n}}{(2n+1)} \cos \frac{(2n+1)\pi \left(x - \frac{l_{x}}{2} \right)}{l_{x}} \exp \left\{ - \left(\frac{(2n+1)\pi}{l_{x}} \right)^{2} D_{x} t \right\} \right) \right] \\ & \times \left(\frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^{n}}{(2n+1)} \cos \frac{(2n+1)\pi \left(y - \frac{l_{y}}{2} \right)}{l_{y}} \exp \left\{ - \left(\frac{(2n+1)\pi}{l_{y}} \right)^{2} D_{y} t \right\} \right) \right] \\ & \times \left(\frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^{n}}{(2n+1)} \cos \frac{(2n+1)\pi \left(z - \frac{l_{z}}{2} \right)}{l_{z}} \exp \left\{ - \left(\frac{(2n+1)\pi}{l_{z}} \right)^{2} D_{z} t \right\} \right) \right] dx dy dz \end{split}$$

Since series in the product are independent, the triple integral may be split into the product of three single integrals:

$$\begin{split} m_{moisture} &= C_{s} \left[l_{x} l_{y} l_{z} - \int_{0}^{l_{x}} \left(\frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^{n}}{(2n+1)} \cos \frac{(2n+1)\pi \left(x - \frac{l_{x}}{2}\right)}{l_{x}} \exp \left\{ - \left(\frac{(2n+1)\pi}{l_{x}} \right)^{2} D_{x} t \right\} \right) dx \\ & \times \int_{0}^{l_{y}} \left(\frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^{n}}{(2n+1)} \cos \frac{(2n+1)\pi \left(y - \frac{l_{y}}{2}\right)}{l_{y}} \exp \left\{ - \left(\frac{(2n+1)\pi}{l_{y}} \right)^{2} D_{y} t \right\} \right) dy \\ & \times \int_{0}^{l_{z}} \left(\frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^{n}}{(2n+1)} \cos \frac{(2n+1)\pi \left(z - \frac{l_{z}}{2}\right)}{l_{z}} \exp \left\{ - \left(\frac{(2n+1)\pi}{l_{z}} \right)^{2} D_{z} t \right\} \right) dz \right] \end{split}$$

Each integral may be evaluated in a similar way to that used in APPENDIX A.1 to give:

$$m_{moisture} = C_s \left[l_x l_y l_z - \left(\frac{8l_x}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left\{ - \left(\frac{(2n+1)\pi}{l_x} \right)^2 D_x t \right\} \right) \\ \times \left(\frac{8l_y}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left\{ - \left(\frac{(2n+1)\pi}{l_y} \right)^2 D_y t \right\} \right) \\ \times \left(\frac{8l_z}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left\{ - \left(\frac{(2n+1)\pi}{l_z} \right)^2 D_z t \right\} \right) \right]$$

Finally, dividing through by the solid mass, $m_{solid} = \rho_{solid} l_x l_y l_z$, and inserting $M_{\infty} = C_s / \rho_{solid}$ gives:

$$\frac{M_t}{M_{\infty}} = 1 - \left(\frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left\{-\left(\frac{(2n+1)\pi}{l_x}\right)^2 D_x t\right\}\right) \\ \times \left(\frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left\{-\left(\frac{(2n+1)\pi}{l_y}\right)^2 D_y t\right\}\right) \\ \times \left(\frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left\{-\left(\frac{(2n+1)\pi}{l_z}\right)^2 D_z t\right\}\right)$$
A.12

Manipulating Equation A.12 further gives:

$$\frac{M_t}{M_{\infty}} = 1 - \left[1 - \left(1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left\{ - \left(\frac{(2n+1)\pi}{l_x} \right)^2 D_x t \right\} \right) \right] \\ \times \left[1 - \left(1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left\{ - \left(\frac{(2n+1)\pi}{l_y} \right)^2 D_y t \right\} \right) \right] \\ \times \left[1 - \left(1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left\{ - \left(\frac{(2n+1)\pi}{l_z} \right)^2 D_z t \right\} \right) \right]$$
A.13

Substituting Equation 2.13 into each term in the product then results in Equation 2.19:

$$\frac{M_t}{M_{\infty}} = 1 - \left(1 - \frac{M_{t,x}}{M_{\infty}}\right) \left(1 - \frac{M_{t,y}}{M_{\infty}}\right) \left(1 - \frac{M_{t,z}}{M_{\infty}}\right)$$
A.14

where $M_{t,x}$, $M_{t,y}$ and $M_{t,z}$ are the respective one dimensional mass absorptions from Equation 2.13 in the x, y and z directions.

A.3 Derivation of Equation 5.1 for composite saturation concentration, C_{sat,c}

The total mass of moisture in a composite sample at saturation, $m_{sat,c}$, is given by the sum of the masses of moisture in the fibre $(m_{sat,f})$, matrix $(m_{sat,m})$ and voids $(m_{sat,v})$:

$$m_{sat,c} = m_{sat,f} + m_{sat,m} + m_{sat,v}$$
A.15

Dividing by the composite volume, V_c , and using the definition of effective concentration in the composite, $C_{sat,c} = m_{sat,c}/V_c$, gives:

$$C_{sat,c} = \frac{1}{V_c} \left(m_{sat,f} + m_{sat,m} + m_{sat,v} \right)$$
A.16

The total volumes of the fibre (V_f) , matrix (V_m) and void (V_v) regions may be included to give:

$$C_{sat,c} = \frac{m_{sat,f}}{V_f} \frac{V_f}{V_c} + \frac{m_{sat,m}}{V_m} \frac{V_m}{V_c} + \frac{m_{sat,v}}{V_v} \frac{V_v}{V_c}$$
A.17

This is a combination of the average concentration in each region $(C_{sat,i} = m_{sat,i}/V_i)$ and the volume fraction of that region $(v_i = V_i/V_c)$. In addition, at saturation, the voids can be assumed to be completely filled with moisture, so the mass of moisture in the voids may be expressed in terms of fluid density, ρ_w , and void volume as $m_{sat,v} = \rho_w V_v$. Equation A.17 becomes:

$$C_{sat,c} = C_{sat,f}v_f + C_{sat,m}v_m + \rho_w v_v$$
 A.18

Finally, the matrix volume fraction can be expressed in terms of the fibre volume fraction and the void fraction as $v_m = 1 - v_f - v_v$ and the equation can be rearranged to give Equation 5.1.

$$C_{sat,c} = C_{sat,f} v_f + C_{sat,m} (1 - v_f - v_v) + \rho_w v_v$$

= $(C_{sat,f} - C_{sat,m}) v_f + [(\rho_w - C_{sat,m}) v_v + C_{sat,m}]$ A.19

APPENDIX B BIDIRECTIONAL FIBRE METHOD DERIVATION

The unit cell used to derive the bidirectional fibre method is shown in Figure B.1. The cell has unit depth with width and height 2a and 2b. The cell is symmetrical about the centreline, the parallel fibres are represented by two strips of width, t, and the perpendicular fibres by a circle of radius, r. It is assumed that flow only occurs in the parallel direction. The concentrations at either side of the cell are C_1 and C_2 . The equivalent resistance network for the cell is show



a. Unit cell



b. Resistance network

Figure B.1 Unit cell and resistance network for derivation of bidirectional fibre method

The flow through each of the parallel fibre sections, Q_f , for unit depth, is given by the definite integral of the Fick's First Law relation, Equation 2.1, from -a to a as:

$$Q_f = -\frac{tD_f}{2a}(C_2 - C_1)$$
B.1

While that through each of the parallel matrix sections, Q_m , is given by a similar integration as:

$$Q_m = -\frac{(b-r-t)D_m}{2a}(C_2 - C_1) = Q_3 - Q_f$$
 B.2

The flow through the central section is treated as the integral of the flows through infinitesimal parallel strips with a section of matrix, a section of fibre of width, s(y), and a second section of matrix, all in series. The flow through one such strip of thickness, dy, is:

$$Q_{2,i} = -\frac{1}{\frac{2(a-s(y)/2)}{D_m dy} + \frac{s(y)}{D_f dy}} (C_2 - C_1) = -\frac{D_m D_f}{D_f (2a-s) + D_m s} (C_2 - C_1) dy$$
B.3

where

$$s(y) = 2\sqrt{r^2 - y^2}$$
B.4

The integrated flow is then:

$$Q_{2} = -D_{m}(C_{2} - C_{1}) \int_{-r}^{r} \frac{dy}{2a + 2\sqrt{r^{2} - y^{2}}(D_{m}/D_{f} - 1)}$$
$$= -D_{m}(C_{2} - C_{1}) \int_{-r}^{r} \frac{dy}{2a + B_{D}\sqrt{r^{2} - y^{2}}}$$
B.5

where

$$B_D = 2\left(\frac{D_m}{D_f} - 1\right)$$

The total flow through the unit cell is the sum of the individual flows:

$$Q_{tot} = 2(Q_f + Q_m) + Q_2$$

= $\left(-\frac{tD_f + (b - r - t)D_m}{a} - \frac{D_m}{B_D}\int_{-r}^{r} \frac{dy}{2a/B_D + \sqrt{r^2 - y^2}}\right)(C_2 - C_1)$
B.6

From the definition of the effective diffusion coefficient, D_c , the total flow is also:

$$Q_{tot} = -\frac{b}{a}D_c(C_2 - C_1)$$
B.7

79

Equating Equations B.6 and B.7 gives:

$$\frac{D_c}{D_m} = \frac{tD_f/D_m + (b - r - t)}{b} + \frac{1}{B_D} \frac{a}{b} \int_{-r}^{r} \frac{dy}{2a/B_D + \sqrt{r^2 - y^2}}$$
$$= \frac{tD_f/D_m + (b - r - t)}{b} + \frac{1}{B_D} \frac{a}{b} \left[\pi - \frac{8a}{\sqrt{4a^2 - B_D^2 r^2}} \left(\operatorname{atan} \frac{2a - B_D r}{\sqrt{4a^2 - B_D^2 r^2}} \right) \right]$$
B.8

Assuming the fibres are arranged in a square array (a = b), the volume fractions of parallel fibres, $v_{f,\parallel}$, and of perpendicular fibres, $v_{f,\perp}$, are defined as:

$$v_{f,\parallel} = \frac{4at}{4ab} = \frac{t}{b}, \qquad v_{f,\perp} = \frac{\pi r^2}{4ab} = \frac{\pi r^2}{4b^2}$$

Equation B.8 becomes:

$$\frac{D_c}{D_m} = 1 + v_{f,\parallel} \left(\frac{D_f}{D_m} - 1 \right) - 2\sqrt{\frac{v_{f,\perp}}{\pi}} + \frac{1}{B_D} \left[\pi - \frac{4}{\sqrt{1 - B_D^2(v_{f,\perp}/\pi)}} \left(\operatorname{atan} \frac{\sqrt{1 - (B_D^2 v_{f,\perp}/\pi)}}{1 + B_D \sqrt{v_{f,\perp}/\pi}} \right) \right]$$
B.9

where:

$$B_D = 2\left(\frac{D_m}{D_f} - 1\right)$$

The fibre direction coefficient, F_D , is introduced to simplify the above relation and is given by:

$$F_D = \frac{v_{f,\parallel}}{v_f}$$

The overall fibre volume fraction is:

$$v_f = v_{f,\parallel} + v_{f,\perp}$$

Thus, the effective diffusivity may be expressed in terms of the direction coefficient and total fibre volume fraction as:

$$\frac{D_c}{D_m} = 1 - v_f F_D \left(\frac{B_D}{B_D + 2} \right) - 2 \sqrt{\frac{v_f (1 - F_D)}{\pi}} + \frac{1}{B_D} \left[\pi - \frac{4}{\sqrt{1 - B_D^2 (v_f (1 - F_D)/\pi)}} \left(\operatorname{atan} \frac{\sqrt{1 - (B_D^2 v_f (1 - F_D)/\pi)}}{1 + B_D \sqrt{v_f (1 - F_D)/\pi}} \right) \right]$$
B.10

APPENDIX C ABSORPTION DATA FROM RASSMANN [46]

C.1 Changing resin system



Figure C.1 Absorption data for 15% volume fraction thermoset samples



Figure C.2 Absorption data for 22.5% volume fraction thermoset samples



Figure C.3 Absorption data for 30% volume fraction thermoset samples

C.2 Changing fibre volume fraction



Figure C.4 Absorption data for epoxy resin samples at three volume fractions



Figure C.5 Absorption data for polyester resin samples at three volume fractions



Figure C.6 Absorption data for vinylester resin samples at three volume fractions

APPENDIX D SAMPLE CALCULATIONS

With the exception of the curve fitting example, all sample calculations are based on an epoxy-kenaf sample with the following data:

Dimensions: $l_x = 4 mm$

$$l_y = l_z = 50 mm$$

Physical properties: $\rho_f = 1500 \ kg/m^3$ $\rho_m = 1139 \ kg/m^3$ $\rho_f = 997 \ kg/m^3$

Diffusion properties:

 $D_f = 25.30 \ mm^2/day$ $D_m = 0.02376 \ mm^2/day$ $D_v = 10 \ mm^2/day$ $M_{\infty,f} = 23.5 \%$ $M_{\infty,m} = 2.41 \%$

Composite properties

$$v_f = 30 \%$$

 $v_v = 5 \%$
 $F_D = 0.01$

D.1 Mass absorption

The plane sheet mass absorption function was tested by comparing its output to a straight line graph of M_t vs. \sqrt{t} .

The slope of the linear curve is given by:

$$Slope = \frac{4M_{\infty}}{l\sqrt{\pi}}\sqrt{D}$$

$$=\frac{4(2.41\%)}{4mm\sqrt{\pi}}\sqrt{\frac{0.02376mm^2}{day}}=0.2096\ \%/day^{\frac{1}{2}}$$

The results of the comparison between linear region and the equilibrium state are shown in Figure D.1. The curve displays linear behaviour at the start and converges to the equilibrium value, indicating that the programmed function behaves as expected.



Figure D.1 Comparison of absorption relation for linear and equilibrium regions

D.2 Curve fitting to predict composite diffusion properties

The curve fitting procedure is illustrated using Asumani's [45] absorption data for 35% weight fraction kenaf-polyester samples in Figure D.2.



Figure D.2 Asumani's [45] absorption data for 35% weight fraction kenaf-polyester samples

Initial guesses of $M_{\infty} = 16\%$ and $D_c = 0.1 \text{ mm}^2/\text{day}$ were made and the initial guess absorption curve shown in Figure D.3 was created using Equation 2.13. For each time sampling point, an error was calculated using Equation 4.1, as shown below. The resulting error values are also plotted in Figure D.3.

 $E_1 = M_{exp,1} - M_{curve,1}$ = 9.54% - 10.30% = -0.77 percentage points



Figure D.3 Asumani's [45] absorption data for 35% weight fraction kenaf-polyester samples, with initial guess absorption curve and error values

For each of the other 10 data points, the error is calculated in a similar way. The sum of the squares of the errors is then obtained:

$$SSE = \sum_{i=1}^{11} E_i^2$$

= (-0.77)² + (-1.49)² + ... + (-1.299)²
= 11.6 (percentage points)²

Finally, the GRG (Generalised Reduced Gradient) nonlinear algorithm [48], was used in Microsoft Excel (2010) solver function, to set SSE to a minimum by modifying the initial guess values for M_{∞} and D_c .

The minimum SSE of 1.68 (percentage points)² was found using values of $M_{\infty} = 16.89\%$ and $D_c = 0.0706 \text{ mm}^2/\text{day}$. The best fit curve and final errors using these values are shown in Figure D.4.



Figure D.4 Asumani's [45] absorption data for 35% weight fraction kenaf-polyester samples, with best fit absorption curve and error values

D.3 Diffusion properties

D.3.1 Saturation concentration

The saturation concentrations for epoxy and fibre are:

$$C_{sat,EP} = \rho_m M_{\infty,m} = 1139 \, kg/m^3 \, (2.41\%) = 27.45 \frac{kg}{m^3}$$
$$C_{sat,f} = \rho_f M_{\infty,f} = 1500 \, kg/m^3 \, (23.5\%) = 352.5 \, kg/m^3$$

The composite saturation concentration is:

$$C_{sat,c} = \rho_f M_{\infty,f} v_f + \rho_m M_{\infty,m} (1 - v_f)$$

= 1500 kg/m³ (23.5%)(30%) + 1139 kg/m³ (2.41%)(1 - 30%)
= 125.0 kg/m³

At saturation, the entire void space is filled with water, so $M_{\infty,v} = 100\%$ and: $C_{sat,v} = \rho_w M_{\infty,v} = 997 \, kg/m^3 \, (100\%) = 997 \, kg/m^3$

D.3.2 Diffusion coefficient

D.3.2.a Thermal resistance analogies

For the resistance analogy, the constant B_D is:

$$B_D = 2\left(\frac{D_m}{D_f} - 1\right) = 2\left(\frac{0.02379 \ mm^2/day}{25.30 \ mm^2/day} - 1\right) = -1.998$$

The effective diffusion coefficient is then:

$$\begin{aligned} \frac{D_{\perp}}{D_m} &= 1 - 2\sqrt{v_f/\pi} + \frac{1}{B_D} \left[\pi - \frac{4}{\sqrt{1 - (B_D^2 v_f/\pi)}} \tan^{-1} \frac{\sqrt{1 - (B_D^2 v_f/\pi)}}{1 + B_D \sqrt{v_f/\pi}} \right] \\ &= 1 - 2\sqrt{30\%/\pi} \\ &+ \frac{1}{-1.998} \left[\pi - \frac{4}{\sqrt{1 - ((-1.998)^2 (30\%)/\pi)}} \tan^{-1} \frac{\sqrt{1 - ((-1.998)^2 (30\%)/\pi)}}{1 - 1.998\sqrt{30\%/\pi}} \right] \\ &= 1 - 0.6180 + \frac{1}{-1.998} \left[\pi - \frac{4}{0.7866} \tan^{-1} \frac{0.7866}{0.3825} \right] \\ &= 1.66 \end{aligned}$$

For the modified resistance analogy, the constant B_W is:

$$B_W = 2\left(\frac{C_{sat,m}D_m}{C_{sat,f}D_f} - 1\right) = 2\left(\frac{27.45 \ kg/m^3(0.02379 \ mm^2/day)}{125.0 \ kg/m^3(25.30 \ mm^2/day)} - 1\right) = -2.000$$

The effective diffusion coefficient is:

$$\begin{aligned} \frac{D_{\perp}}{D_m} &= \left(1 - 2\sqrt{v_f/\pi}\right) \frac{C_{sat,m}}{C_{sat,e}} + \frac{C_{sat,m}}{C_{sat,e}} \frac{1}{B_W} \left[\pi - \frac{4}{\sqrt{1 - \left(B_W^2 v_f/\pi\right)}} \tan^{-1} \frac{\sqrt{1 - \left(B_W^2 v_f/\pi\right)}}{1 + B_W \sqrt{v_f/\pi}}\right] \\ &= \left(1 - 2\sqrt{30\%/\pi}\right) \frac{27.45 \, kg/m^3}{125.0 \, kg/m^3} + \frac{27.45 \, kg/m^3}{125.0 \, kg/m^3} \frac{1}{-2.000} \\ &\times \left[\pi - \frac{4}{\sqrt{1 - \left((-2.000)^2 (30\%)/\pi\right)}} \tan^{-1} \frac{\sqrt{1 - \left((-2.000)^2 (30\%)/\pi\right)}}{1 - 2.000\sqrt{30\%/\pi}}\right] \\ &= (1 - 0.6180) 0.2196 + 0.2196 \frac{1}{-2.000} \left[\pi - \frac{4}{0.7862} \tan^{-1} \frac{0.7862}{0.3821}\right] \end{aligned}$$

= 0.364

D.3.2.b Three- and four-phase models

The constant, ψ , for the three-phase model is:

$$\psi = \frac{C_{sat,f}}{C_{sat,m}} \frac{D_f}{D_m} = \frac{352.5 \ kg/m^3}{27.45 \ kg/m^3} \frac{25.30 \ mm^2/day}{0.02379 \ mm^2/day} = 13656$$

The effective diffusion coefficient for the three-phase model is:

$$\frac{D_{eff}}{D_m} = \frac{(1 - v_f) + \psi(1 + v_f)}{(1 + v_f) + \psi(1 - v_f)}$$
$$= \frac{(1 - 30\%) + 13656(1 + 30\%)}{(1 + 30\%) + 13656(1 - 30\%)} = 1.86$$

The constants for the four-phase model are:

$$k = \frac{v_v + v_f}{v_f} = \frac{5\% + 30\%}{30\%} = 1.167$$

$$\alpha_{mv} = \frac{C_{sat,v}}{C_{sat,m}} = \frac{997 \ kg/m^3}{27.45 \ kg/m^3} = 36.32$$

$$\alpha_{fv} = \frac{C_{sat,f}}{C_{sat,v}} = \frac{325.5 \ kg/m^3}{997 \ kg/m^3} = 0.3265$$

$$\Phi = \alpha_{mv} \frac{D_v}{D_m} = 36.32 \frac{10 \ mm^2/day}{0.02376 \ mm^2/day} = 15 \ 286$$

$$\Psi = \alpha_{fv} \frac{D_f}{D_m} = 0.3265 \frac{25.30 \ mm^2/day}{0.02376 \ mm^2/day} = 347.7$$

The effective diffusion coefficient is:

$$\begin{aligned} \frac{D_{eff}}{D_m} &= \frac{(1-kv_f)[1+k+\alpha_{mv}(\Psi/\Phi)(k-1)] + (1+kv_f)[\Phi(k-1)+\alpha_{mv}\Psi(k+1)]}{(1+kv_f)[1+k+\alpha_{mv}(\Psi/\Phi)(k-1)] + (1-kv_f)[\Phi(k-1)+\alpha_{mv}\Psi(k+1)]} \\ &= \left\{ \left(1-1.167(30\%)\right) \left[2.167+36.32\left(\frac{347.7}{15286}\right)(0.167)\right] \\ &+ \left(1+1.167(30\%)\right)[15286(0.167)+36.32(347.7)(2.167)] \right\} \end{aligned}$$

$$\div \left\{ \left(1 + 1.167(30\%) \right) \left[2.167 + 36.32 \left(\frac{347.7}{15286} \right) (0.167) \right] \right. \\ \left. + \left(1 - 1.167(30\%) \right) \left[15286(0.167) + 36.32(347.7)(2.167) \right] \right\} \\ \left. = \frac{\left(0.65 \right) \left[2.305 \right] + \left(1.35 \right) \left[29918 \right]}{\left(1.35 \right) \left[2.305 \right] + \left(0.65 \right) \left[29918 \right]} = 2.08$$

D.3.2.c Self-consistent model

The prediction function code for the self-consistent method is checked by manually performing the calculation for two iterations (N = 2). The two partial volume fractions are:

$$\Delta v_{f,n} = \frac{v_f}{N - (n-1)v_f}$$
$$\Delta v_{f,1} = \frac{30\%}{2 - (1-1)30\%} = 0.15$$
$$\Delta v_{f,2} = \frac{30\%}{2 - (2-1)30\%} = 0.1765$$

The first iteration step gives:

$$\begin{split} \frac{D_{eff,1}}{D_m} &= \frac{1}{2} \left(\frac{D_f}{D_m} \left(2v_{f,1} - 1 \right) + \left(1 - 2v_{f,1} \right) \right) \\ &+ \frac{1}{2} \left(\sqrt{\frac{4D_f}{D_m} + \left[\frac{D_f}{D_m} \left(1 - 2v_{f,1} \right) + \left(2v_{f,1} - 1 \right) \right]^2} \right) \right) \\ &= \frac{1}{2} \left(\frac{25.30 \ mm^2 / day}{0.02376 \ mm^2 / day} \left(2(0.15) - 1 \right) + \left(1 - 2(0.15) \right) \right) \\ &+ \frac{1}{2} \sqrt{\left(\frac{4(25.30 \ mm^2 / day)}{0.02376 \ mm^2 / day} + \left[\frac{25.30 \ mm^2 / day}{0.02376 \ mm^2 / day} \left(1 - 2(0.15) \right) + \left(2(0.15) - 1 \right) \right]^2 \right)} \\ &= \frac{1}{2} \left(1064.8(-0.7) + (0.7) \right) + \frac{1}{2} \left(\sqrt{4259.3 + [1064.8(0.7) + (-0.7)]^2} \right) \\ &= 1.4324 \\ D_{eff,1} = 0.03403 \ mm^2 / day \end{split}$$

The second iteration step gives:

$$\begin{split} \frac{D_{eff,2}}{D_{eff,1}} &= \frac{1}{2} \left(\frac{D_f}{D_{eff,1}} \left(2\Delta v_{f,2} - 1 \right) + \left(1 - 2\Delta v_{f,2} \right) \right) \\ &+ \frac{1}{2} \sqrt{\frac{4D_f}{D_{eff,1}}} + \left[\frac{D_f}{D_{eff,1}} \left(1 - 2\Delta v_{f,2} \right) + \left(2\Delta v_{f,2} - 1 \right) \right]^2} \\ &= \frac{1}{2} \left(\frac{25.30 \ mm^2 / day}{0.03403 \ mm^2 / day} \left(2(0.1765) - 1 \right) + \left(1 - 2(0.1765) \right) \right) \\ &+ \frac{1}{2} \sqrt{\frac{4(25.30 \ mm^2 / day}{0.03403 \ mm^2 / day}} + \left[\frac{25.30 \ mm^2 / day}{0.03403 \ mm^2 / day} \left(1 - 2(0.1765) \right) + \left(2(0.1765) - 1 \right) \right]^2 \\ &= \frac{1}{2} \left(743.5 \left(-0.647 \right) + \left(0.647 \right) \right) + \frac{1}{2} \sqrt{2973 + [743.5 \left(0.647 \right) + \left(-0.647 \right)]^2} \\ &= 1.5422 \\ D_{eff,2} &= 0.05248 \ mm^2 / day \\ \frac{D_{eff}}{D_m} &= 2.21 \end{split}$$

D.3.2.d Bidirectional fibre model

The constants for the bidirectional fibre model are:

$$B_D = -1.998$$

The effective diffusion coefficient is:

$$\frac{D_c}{D_m} = 1 - v_f F_D \left(\frac{B_D}{B_D + 2}\right) - 2\sqrt{\frac{v_f (1 - F_D)}{\pi}} + \frac{1}{B_D} \left[\pi - \frac{4}{\sqrt{1 - B_D^2 (v_f (1 - F_D)/\pi)}} \left(\operatorname{atan} \frac{\sqrt{1 - (B_D^2 v_f (1 - F_D)/\pi)}}{1 + B_D \sqrt{v_f (1 - F_D)/\pi}} \right) \right]$$

$$= 1 - 0.3\% \left(\frac{-1.998}{-1.998 + 2}\right) - 2\sqrt{\frac{29.7\%}{\pi}}$$
$$+ \frac{1}{-1.998} \left[\pi - \frac{4}{\sqrt{1 - \left(\frac{1.998^2(29.7\%)}{\pi}\right)}} \operatorname{atan} \frac{\sqrt{1 - \left(\frac{1.998^2(29.7\%)}{\pi}\right)}}{1 - 1.998\sqrt{\frac{29.7\%}{\pi}}} \right]$$

$$= 1 + 2.997 - 0.6149 - \frac{1}{1.998} \left[\pi - \frac{4}{0.7891} \operatorname{atan} \frac{0.7891}{0.3857} \right]$$

= 4.64
APPENDIX E VBA CODE FOR PLANE SHEET MASS ABSORPTION

Option Explicit

```
' Diffusion coefficient
Private D As Double
                           ' Plane sheet thickness
' Plane sheet geometry constant
Private L As Double
Private Psi As Double
                            ' Time
Private t As Double
Private convmax As Double
                           ' Convergence ratio that must be reached before series
                            ' sum is considered converged
                            ' Maximum allowable iterations for series sum
Private nmax As Integer
                           ' Minimum required converged iterations for series sum
Private nmin As Integer
' Default value if convmax not explicitly specified
Private Const convmaxdef As Double = 0.0000001
' Default value if nmax not explicitly specified
Private Const nmaxdef As Integer = 1000
' Default value if nmin not explicitly specified
Public Const nmindef As Integer = 2
Private Const Pi As Double = 3.14159265358979
Function MassFickPS(L, t, D, Optional convmax, Optional nmin, Optional nmax)
  ' Calculates the relative mass of diffusing substance entering or leaving plane
  ' sheet (thickness, L) with uniform initial concentration, exposed to diffusing
  ' substance on one or both sides. Result is expressed relative to the amount of
  ' substance that has entered crossing after infinite time / at equilibrium.
      L - thickness of sheet, t - time
      D - Diffusion coefficient
       convmax - convergence ratio (default 1E-7)
      nmin - minimum iterations for which convergence criteria must be below
             convmax (default 2)
      nmax - max iterations (default 1000)
      Based on relations described in Crank, J., 'The Mathematics of Diffusion',
       Oxford University Press, 2nd Ed, 1975
       Written by E.D. Carman as part of MSc research at Wits University -
  ,
       25/3/2011
 Dim sumC1 As Variant
  ' Return result when time = 0
  If t = 0 Then
   MassFickPS = 0
   Exit Function
  ElseIf t < 0 Then
   MassFickPS = "Error: t < 0"
   Exit Function
  End If
  ' Calculate PsiPS
  Psi = Pi ^ 2 * D / L ^ 2
  ' Check for custom convergence criteria, otherwise assign defaults
  If IsMissing(convmax) Then
   convmax = convmaxdef
  End
  If IsMissing(nmin) Then
   nmin = nmindef
  End If
  If IsMissing(nmax) Then
   nmax = nmaxdef
  End If
  If nmin > nmax / 10 Then
   MassFickPS = "Error: nmin > nmax/10"
  ElseIf nmin = 0 Then
   MassFickPS = "Error: nmin must be >0"
  End T
  ' Calculate the series sum
  sumC1 = sumC(Psi, t, convmax, nmin, nmax)
```

```
' Check whether the sum has converged. If not, return the sumB error string
  If IsNumeric(sumC1) Then
   MassFickPS = 1 - 8 / Pi ^ 2 * sumC1
  Else
   MassFickPS = sumC1
  End If
End Function
Private Function sumC(Psi, t, convmax, nmin, nmax)
   ' Calculates the series sum. Convergence determined by specified criterion
  Dim m As Integer ' Sum index / Number of completed iterations
  Dim C As Double
  Dim convC As Double
  Dim convTest() As Integer ' Arrays used to store convergence values
  Dim convArray() As Double
  ' Initialise variables
  m = 0
  sumC = 0
  ReDim convArray(1 To nmin) As Double
  ReDim convTest (1 To nmin) As Integer
  ' Loop until convergence criteria is met for 'nmin' consecutive iteration or
  ' until maximum allowed iterations are reached
  Do
   C = 1 / (2 * m + 1) ^ 2 * Exp(-1 * (2 * m + 1) ^ 2 * Psi * t)
   sumC = sumC + C
    m = m + 1
    convArray((m Mod nmin) + 1) = Abs(C / sumC) ' Assigns convergence value to
      ' some position in array. Mod ensures array contains only last nmin values
    ' Convergence test.
      ' All array values initially at 0.
      ' Values only change to 1 if the convergence test is satisfied for that
      ' iteration. True = -1, but the negative is used to ensure the product
      ' retains the same sign for even and odd values of nmin
      ' Previous nmin iterations stored
    convTest((m Mod nmin) + 1) = -(convArray((m Mod nmin) + 1) <= convmax) ' Tests</pre>
      ' whether Abs\left(C \ / \ sumC
ight) is less than the convergence value. Assigns 1 if it
      ' is, 0 if not
  Loop Until -WorksheetFunction.Product(convTest) Or m >= nmax ' Product is only
    '-(1) (true) when all entries in array are 1, otherwise it's 0
  'Check convergence
  If Not -WorksheetFunction.Product(convTest) Then convC =
          WorksheetFunction.Average(convArray)
    sumC = "SumC unconverged after " & nmax & " iterations. convC = " &
           Format(convC, "Scientific") & ", convCmax = " &
           Format(WorksheetFunction.max(convArray), "Scientific")
  End If
```

```
End Function
```

APPENDIX F VBA CODE FOR ITERATIVE SELF-CONSISTENT METHOD

Option Explicit

```
Function Deff SC(Dm As Variant, Df As Variant, vf As Variant, N As Variant)
   Implements the iterative self-consistent model to predict effective diffusion
  ' coefficients (Deff) for a composite, based on its fibre (Df) and matrix (Dm)
  ' diffusion coefficients and its fibre volume fraction (vf). The number of
  ' iterations required, N, is also specified.
  ' Based on relations described in Gueribiz D. et al., "Homogenization of
  ' moisture diffusing behavior of composite materials with impermeable or
  ' permeable fibers - application to porous composite materials", Journal of
  ' Composite Materials, vol. 43, no. 12, June 2009, pp. 1391-1408.
  ' Written by E.D. Carman as part of MSc research at Wits University - 25/7/2011
  Dim DmD As Double
  Dim DfD As Double
  Dim vfD As Double
  Dim NI As Integer
  Dim delvfn As Double
  Dim Deff_old As Double
  Dim i As Integer
  ' Convert inputs to correct type
  DmD = CDbl(Dm)
  DfD = CDbl(Df)
  vfD = CDbl(vf)
  NI = CInt(N)
  ' Always have at least one iteration
  If NI < 1 Then NI = 1
 Deff SC = DmD
  For i = 1 To NI
   Deff_old = Deff_SC
   delvfn = vfD / (NI - (i - 1) * vfD)
   Deff SC = Deff SC root (Deff old, DfD, delvfn)
  Next i
End Function
Private Function Deff_SC_root(Dm As Double, Df As Double, vf As Double)
  ' Implements the single iteration version of the S-C model
  Dim Dfm As Double
  Dim Root As Double
 Dfm = Df / Dm
```

Root = Sqr(4 * Dfm + (Dfm * (1 - 2 * vf) + (2 * vf - 1)) ^ 2) Deff_SC_root = 0.5 * Dm * (Dfm * (2 * vf - 1) + (1 - 2 * vf) + Root) End Function