Gas Transport and Void Evolution in Composite Prepregs

by

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Abstract

Out-of-autoclave (OOA) processing of prepregs represents a promising low cost alternative to expensive autoclave processing, which today is the standard method for producing high-quality CFRP parts such as aerospace structures; however, OOA processes have a greater potential to experience problems with voids than autoclave processes do. Understanding the evolution of voids during the prepreg process, and the OOA prepreg process in particular, is a key to robust and low cost processing that can produce high quality composite parts with low porosity.

The evolution of voids in prepregs is best understood as the result of interacting transport mechanisms during the debulk and cure processing steps. The most important such mechanisms are the in-plane flow of gasses through an interconnected network of voids, the diffusion of dissolved moisture within the resin, the sorption and desorption of moisture into and out of the resin, and the flow of resin into the void spaces.

A large experimental project has been carried out to experimentally measure the effect of varying the parameters of the OOA process on the porosity levels of cured parts. The results of the experiments show that factors like part size, moisture content, and debulk time influence the porosity levels of parts produced. The governing transport mechanisms have been investigated and characterized, and a numerical model capable of simulating the simultaneous action of these interacting mechanisms is proposed.

The numerical model was validated by comparison with experimental measurements of moisture content during a debulk, and it was shown that the proposed model is able to predict the measured values with reasonable accuracy. A method of estimating part porosity using the numerical model was proposed and its results were compared with the experimental results. The knowledge presented is

ii

then used to explain observed experimental results published by other authors and to suggest a novel processing technique.

Lay Summary

Composite materials like carbon-fiber offer many advantages over metallic materials like aluminum that make them very attractive to aircraft manufacturers and other industries where weight-savings is important. Currently, high-quality composite parts are produced using a pressurized oven known as an autoclave which applies high pressure during processing of the parts. This is done to reduce or eliminate any gas bubbles within the part that can reduce the strength and other desirable properties of the material. Owning and operating an autoclave is very expensive though, and it is desired to eliminate the need for an autoclave in composite part production. This work aims to build a scientific understanding of how gas bubbles form and grow in composite materials. It is hoped that this understanding will lead to methods of producing composite parts without the need for the autoclave.

Preface

This thesis consists of research conducted by James Kay at the University of British Columbia under the supervision of Dr. Goran Fernlund.

All the research presented in this thesis was conducted by the author; however, preliminary work that set the groundwork for the research presented was conducted in association with Leyla Farhang and Kevin Hsiao. The quantification of surface porosity by image analysis is based on a technique developed by Martin Roy.

The experimental work discussed in Chapter 6 has not been published previously, but the experimental procedure as well as the results of similar preliminary experiments were published in:

- Kay, J., Fernlund, G. (2012.) "*Processing Conditions and Voids in Out of Autoclave Prepregs*" and presented at the SAMPE 2012 Conference, May 2012, Baltimore, USA
- Kay, J., Farhang, L., Hsiao, K., Fernlund, G. "Effect of Process Conditions on Porosity in Out-ofautoclave Prepreg Laminates", Presented by Göran Fernlund at the ICCM 18 Conference, August 2011, Jeju Island, Korea.
- Hsiao, K., Kay, J., Fernlund, G. (2011.) "Gas Transport and Water Evaporation in Out of Autoclave Prepregs", Presented by Kevin Hsiao at the CANCOM 2011 Conference, September 2011, Montreal, Canada.

The sorption data shown in Figure 5.3 was also previously published in the 2011 paper above.

All analysis of the research data contained in this thesis was conducted by the author.

Table of Contents

Ab	stra	act.			ii	
Lay	ay Summaryiv					
Pre	efac	ce			v	
Та	ble	of C	Conte	ents	vi	
Lis	t of	Tal	oles .		x	
Lis	t of	^F Fig	ures		xi	
Glo	ossa	ary.			‹v	
Ac	kno	wle	dger	nentsxv	/ii	
1	h	ntro	duct	ion	1	
	1.1		Histo	ory	1	
	1.2		Proc	essing of Prepregs	2	
2	L	iter	ature	e Review1	0	
	2.1		Phys	ical Mechanisms1	.0	
	2	2.1.1	_	Gas Flow	.1	
	2	2.1.2	2	Sorption of Volatiles1	.7	
	2	2.1.3	5	Resin Flow	20	
	2.2		Porc	sity Prediction2	22	
3	C	Dbje	ctive	25	24	
	3.1		Obje	ectives and Goals2	24	
	3.2		Task	s2	24	
4	Т	ran	sport	t Mechanisms Framework: Interaction and Time Scales	26	
	4.1		Simp	plified Microstructure Model2	26	
	4.2		Inte	raction of Transport Mechanisms2	28	
	4.3		Esta	blishing Approximate Time Scales	31	
	4	.3.1	_	Time Scale for Dry Gas Flow	31	
	4	.3.2	2	Time Scale for Moisture Vapour Flow	32	
	4	.3.3	}	Time Scale for Diffusion	3	
	4	.3.4	Ļ	Time Scale for Resin Infiltration	35	
5	E	xpe	rime	nts: Moisture Sorption	10	

	5.1	Con	trolling Relative Humidity	42
	5.2	Moi	sture and Relative Humidity	43
	5.3	Effe	ct of Pressure on Equilibrium	45
	5.4	Effe	ct of Temperature on Equilibrium	46
	5.5	Moi	sture Sorption in Open Air	49
	5.6	Moi	sture Content During Debulk	56
6	Ex	perime	ents: Variability In Raw Material	60
	6.1	Vari	ability Within a Roll of Material	60
	6.1	l.1	Initial Thickness Variations	60
	6.1	L.2	Initial Moisture Content Variations	65
	6.2	Vari	ability Between Rolls of Material	67
7	Ex	perime	ents: Porosity and Process Parameters	68
	7.1	The	Problem of Variability	71
	7.2	Ove	rcoming Experimental Obstacles	72
	7.3	Expe	eriment Parameters	73
	7.4	Expe	erimental Methods	73
	7.4	1.1	Ply Cutting and Layup	74
	7.4	1.2	Moisture Conditioning and Humidity Control	75
	7.4	1.3	Debulk and Cure	76
	7.4	1.4	Bulk Porosity Quantification	80
	7.4	1.5	Surface Porosity Quantification	85
	7.5	Expe	erimental Results	88
	7.5	5.1	Conditioned Moisture Contents	88
	7.5	5.2	Bulk Porosity	88
	7.5	5.3	Surface Porosity	95
	7.5	5.4	Effect of Resin Bleed and Resin Pressure Loss1	.02
	7.5	5.5	Case Studies of Problems Encountered in Debulk and Cure1	09
8	Sca	aling R	elationships1	.19
9	Nu	imerica	al Model1	.23
	9.1	Мос	del Derivation1	.29
	9.2	Мос	del output1	.31
	9.3	Мос	del Verification1	.34

ç	9.4	(Compari	ison with Experimental Results	136
ç	9.5	I	Model B	Behavior	139
ç	9.6	I	Porosity	Estimation	143
	9.	.6.1	Con	mparison to Experimental Results: Average Porosity	145
	9.	.6.2	Con	mparison to Experimental Results: Porosity Profiles	148
	9.	.6.3	Disc	connected Void Component Porosity Estimation Model	150
	9.	.6.4	Disc	cussion of Porosity Estimation Models	153
ç).7		Small La	minates and Resin Bleed	154
ç	9.8	I	imitatic	ons and Future Improvements	155
10	Ρ	roce	ssing St	rategies	157
1	.0.1	LI	Dry Gas	Flush	157
1	.0.2	2	leated [Debulk	161
11	D	iscu	ssion		166
1	.1.1	L	Agreeme	ent between Model and Experiments	166
1	1.2	<u>, v</u>	/ariabili	ty	167
1	1.3	3	Bulk and	d Surface Porosity	169
1	.1.4	1 (Generali	ization of Experimental Results	169
12	Si	umr	nary and	d Contributions	171
13	F	utur	e Work.		174
Bib	liog	grap	hy		176
Арј	ben	dice	s		183
Ap	ben	dix	A - Nonc	dimensionalization of Darcy's Law for Gas Flow	183
Арј	ben	dix	3 - Nonc	dimensionalization of Fick's Law	186
Ap	ben	dix	C - Nonc	dimensionalization of Darcy's Law for Resin Flow	190
(2.1	Assı	iming Co	onstant Viscosity	190
(2.2	Alte	rnative ((Flow Index) Approach	192
Арј	ben	dix	D - Fixed	d Point Humidity (FPH) Salt Solutions	194
Арј	ben	dix	E - Calcu	ulation of Input Parameters for Numerical Model	195
Арј	ben	dix	- Deriv	vation of Numerical Model	199
Арј	ben	dix	G - Impl	lementation of Numerical Model in MATLAB	212
(5.1	Initi	al Condi	itions	216
(5.2	Bou	ndary Co	onditions	217

Appendix H - MATLAB Code for Numerical Model	219
Appendix I - Diffusion of Moisture Through Air and Resin	222

List of Tables

Table 2.1: Typical measured permeability values	
Table 2.2: Range of parameters for calculation of Reynolds number in gas flow	14
Table 2.3: Range of parameters for mean free path calculation	16
Table 2.4: Range of parameters for calculation of Reynolds number of resin flow	21
Table 4.1: Comparison of real prepreg with simplified microstructure model	
Table 2: Humidity Control Media	42
Table 5.3: Diffusion Coefficients	55
Table 6.1: Components of variance in thickness data	63
Table 7.1: Parameters and camera settings	86
Table 7.2: Intercept calculated from different data sets	97
Table 7.3: Resin bled into cork dam	104
Table 7.4: Comparison of resin bleed estimates	105
Table 9.1: Current understanding of void evolution during cure	
Table 9.2: Dependent variables in model	
Table 9.3: Input parameters required in model	128
Table 9.4: Procesing parameters	
Table 9.5: Equivalent debulk time while varying permeability and diffusion coefficient	142
Table 9.6: Porosity in 0.1m laminates	155
Table E.1: Input values for diffusion parameter calculation in MTM45-1/5HS prepreg	

List of Figures

Figure 1.1: Macro-photograph of prepreg	3
Figure 1.2: Schematic of the Prepreg Process	4
Figure 1.3: Sources of voids in the prepreg process	6
Figure 1.4: Typical prepreg microstructure	7
Figure 1.5: Taxonomy of voids	7
Figure 2.1: Gas Flow	11
Figure 2.2: Initial prepreg microstructure	12
Figure 2.3: Desorption of volatiles	17
Figure 2.4: Resin flow	20
Figure 2.5: Resin Flow	21
Figure 4.1: Real and Simplified Prepreg Microstructure	27
Figure 4.2: Resin Infiltration	27
Figure 4.3: Physical mechanisms operating during OOA prepreg processing	29
Figure 4.4: Interaction of transport mechanisms	30
Figure 4.5: Time scales for moisture diffusion and flow of dry gas and moisture vapour. (Best in colou	r
when available)	34
Figure 4.6: Initial viscosity of MTM45-1 resin	35
Figure 4.7: Viscosity over constant temperature debulk	36
Figure 4.8: Time scale for resin infiltration	38
Figure 5.1: Concentration of air and water molecules in prepreg	41
Figure 5.2: Example of a humidity conditioning container	43
Figure 5.3: Relationship between equilibrium moisture content and relative humidity at room	
temperature	44
Figure 5.4: Effect of ambient pressure on moisture equilibrium	46
Figure 5.5: Parabolic sorption curves at various temperatures	47
Figure 5.6: Parameter k1 as a function of temperature	48
Figure 5.7: Equilibrium moisture content as a function of water vapour pressure	49
Figure 5.8: G in time domain	51
Figure 5.9: G in root time domain	51
Figure 5.10: Cup used in neat resin moisture absorption experiments	52
Figure 5.11: Analytical balance with humidity control jig	53
Figure 5.12: Sorption curve for prepreg in root-time domain	54
Figure 5.13: Sorption curve for neat resin in root-time domain	54
Figure 5.14: Comparison of sorption data for prepreg samples with Fickian Model	56
Figure 5.15: Arrangement under vacuum bag	57
Figure 5.16: Moisture content after debulk	58
Figure 5.17: Moisture content profiles after debulk	59
Figure 6.1: Strips Cut from Material Roll	60
Figure 6.2: Thickness Variation Along Prepreg Roll	61

Figure 6.3: Histogram Plot of Remaining Thickness Variations (σ =6.5 μ m)	62
Figure 6.4: Initial thickness variations along roll edges	64
Figure 6.5: Initial Moisture Content Variation Over Prepreg Roll	65
Figure 6.6: Histogram Plot of Remaining Moisture Content Variations (σ =0.02%MC)	66
Figure 7.1: Categorization of Parameters	68
Figure 7.2: Qualitative relationships	70
Figure 7.3: Relationship between porosity and resin pressure	70
Figure 7.4: Ply cutting	74
Figure 7.5: Vacuum bagging arrangement (nylon bag not shown for clarity)	78
Figure 7.6: Photograph of typical vacuum bag arrangement	79
Figure 7.7: 1m laminate cut into 10 pieces (*this piece omitted from porosity measurements)	
Figure 7.8: Thickness Contribution of Composite and Voids	83
Figure 7.9: Porosity measured using Optical Microscopy and Density methods	85
Figure 7.10: Photographic setup for surface porosity quantification	86
Figure 7.11: Quantification of surface porosity	87
Figure 7.12: Average bulk porosity, 75% Relative Humidity	89
Figure 7.13: Average bulk porosity, 33% Relative Humidity	90
Figure 7.14: Bulk porosity profiles in 1m parts exposed to 75% relative humidity	91
Figure 7.15: Bulk porosity profiles in 1m parts exposed to 33% relative humidity	92
Figure 7.16: Bulk porosity profiles in 0.3m parts exposed to 75% relative humidity	92
Figure 7.17: Bulk porosity profiles in 0.3m parts exposed to 33% relative humidity	93
Figure 7.18: Example of bulk porosity decrease at most distant data point in 1m parts	94
Figure 7.19: Average surface porosity, 75% Relative Humidity	95
Figure 7.20: Average surface porosity, 33% Relative Humidity	96
Figure 7.21: Relationship between bulk and surface porosity	97
Figure 7.22: Surface porosity profiles in 1m parts exposed to 75% relative humidity	98
Figure 7.23: Surface porosity profiles in 1m parts exposed to 33% relative humidity	99
Figure 7.24: Surface porosity profiles in 0.3m parts exposed to 75% and 33% relative humidity	99
Figure 7.25: Comparison of bulk and surface porosity profiles (1m, 75% relative humidity, 0.5hr d	lebulk,
part A)	100
Figure 7.26: Comparison of bulk and surface porosity profiles (1m, 75% relative humidity, 0.5hr d	lebulk,
part B)	100
Figure 7.27: Comparison of bulk and surface porosity profiles (1m, 75% relative humidity, 0.5hr d	lebulk,
part C)	100
Figure 7.28: Comparison of bulk and surface porosity profiles (1m, 75% relative humidity, 4hr del	bulk,
part A)	101
Figure 7.29: Comparison of bulk and surface porosity profiles (1m, 75% relative humidity, 4hr del	bulk,
part B)	101
Figure 7.30: Comparison of bulk and surface porosity profiles (1m, 75% relative humidity, 4hr del	bulk,
part C)	101
Figure 7.31: Measurement of resin bled into peel ply	103
Figure 7.32: Measurement of resin bled into cork dam	104

Figure 7.33: Areal density of experimental parts grouped by length	106
Figure 7.34: Bulk porosity, 75% relative humidity	107
Figure 7.35: Bulk porosity, 33% Relative Humidity	107
Figure 7.36: Surface porosity, 75% Relative Humidity	108
Figure 7.37: Surface porosity, 33% Relative Humidity	108
Figure 7.38: Effect of leak at vacuum fittings on bulk porosity profiles (1m, 75% relative humidity,	24hr
debulk)	110
Figure 7.39: : Effect of leak at vacuum fittings on surface porosity profiles (1m, 75% relative humic	dity,
24hr debulk)	111
Figure 7.40: Arrows indicate locations where layup was lifted from the tool part way through the	cure
cycle	112
Figure 7.41: Tool-side surfaces of parts with regions showing a rough surface finish highlighted	113
Figure 7.42: Comparison of morphology of surface porosity on tool side of parts A and C	114
Figure 7.43: Comparison of bulk porosity profiles of normal parts with parts A, B, C (1m, 75% relat	ive
humidity, 24hr debulk)	115
Figure 7.44: Stray fibers bridging the vacuum seal	115
Figure 7.45: Effect of compromised vacuum seal on bulk porosity profile (1m, 75% relative humidi	ity,
24hr debulk)	116
Figure 7.46: Effect of compromised vacuum seal on surface porosity profile (1m, 75% relative hun	nidity,
24hr debulk)	116
Figure 7.47: Effect of minor vacuum leak on bulk porosity profile (0.3m, 33% relative humidity, 4h	r
debulk)	117
Figure 7.48: Effect of minor vacuum leak on surface porosity profile (0.3m, 33% relative humidity,	4hr
debulk)	118
Figure 7.49: Effect of minor vacuum leak on porosity levels of 0.1m parts (33% relative humidity, 4	4 hr
debulk)	118
Figure 8.1: Linear fit to measured bulk porosity vs ζ for laminates exposed to 75% relative humidit	y120
Figure 8.2: Linear fit to bulk porosity vs ζ for laminates exposed to 33% relative humidity	121
Figure 8.3: Linear fit to surface porosity vs ζ for laminates exposed to 75% relative humidity	121
Figure 8.4: Linear fit to surface porosity vs ζ for laminates exposed to 33% relative humidity	122
Figure 9.1: Element considered in the model	125
Figure 9.2: Physical meaning of parameter beta	126
Figure 9.3: Model output for dry gas pressure (with inset of initial ten minutes)	132
Figure 9.4: Model output for moisture vapour pressure (with inset of first ten minutes)	132
Figure 9.5: Model output for resin infiltration parameter	133
Figure 9.6: Model output for resin moisture content	133
Figure 9.7: Model output for validation	135
Figure 9.8: Measured and predicted moisture content after debulk based on baseline diffusion rate	te 136
Figure 9.9: Measured and predicted moisture content profiles after debulk based on baseline difference of the second seco	usion
rate	137
Figure 9.10: Measured and predicted moisture content with diffusion rate decreased	138
Figure 9.11: Measured and predicted moisture content profiles with diffusion rate decreased	138

Figure 9.12: Resin moisture content over a debulk when permeability and diffusion coefficie	nt are varied
Figure 9.13: Resin movement during cure and debulk	
Figure 9.14: Comparison of estimated and measured bulk porosity levels for laminates exposed relative humidity	sed to 75%
Figure 9.15: Comparison of estimated and measured bulk porosity levels for laminates exposed relative humidity	sed to 33% 147
Figure 9.16: Comparison of estimated and measured bulk porosity profiles, 1m parts expose relative humidity	d to 75% 148
Figure 9.17: Comparison of estimated and measured bulk porosity profiles, 1m parts expose relative humidity	d to 33%
Figure 9.18: Comparison of estimated and measured bulk porosity profiles, 0.3m parts exposed relative humidity	sed to 75% 149
Figure 9.19: Comparison of estimated and measured bulk porosity profiles, 0.3m parts exposed relative humidity	sed to 33% 150
Figure 9.20: Improved porosity estimates using DVC model for laminates exposed to 75% rel humidity	ative 152
Figure 9.21: Improved porosity estimates using DVC model, 0.3m parts exposed to 75% relat	ive humidity
Figure 10.1: Simulated Dry Gas Flush	
Figure 10.2: Vacuum bag arrangement for dry gas flush experiment	
Figure 10.3: Moisture removed during normal debulk vs dry gas flush	160
Figure 10.4: Effect of Temperature on Time Scales	163
Figure 10.5: Effect of Temperature of Moisture Removal	164
Figure A.1: Pressure profiles (nondimensionalized Darcy's law)	184
Figure A.2: Fraction of gas remaining (nondimensionalized Darcy's law)	
Figure B.1: Concentration profiles (nondimensionalized Fick's law)	
Figure B.2: Fraction of solute remaining (nondimensionalized Fick's law)	189
Figure C.1: Relationship between gamma and tau	192
Figure D.1: Fixed Point Humidity vs Temperature	194
Figure E.1: Diffusion of moisture in resin film	196
Figure F.1: Representative Volume Element	199
Figure F.2: Physical meaning of parameter gamma	200
Figure F.3: Resin infiltration in a representative volume element	209
Figure I.1: Moisture diffusion through epoxy and air	222

Glossary

5-harness satin: See satin weave

Autoclave: A pressurized oven used to cure composite parts under high pressure.

Bleed: The flow of resin out of a prepreg during cure.

Breathe-out distance: The distance that gas must travel through a prepreg laminate to reach the vacuum system.

Breathing edge: An edge of a laminate where it is exposed to the vacuum system.

Cold flow: The flow of resin at room temperature, typically during the debulk processing step, as opposed to the flow of resin at eleveted temperatures as during the cure processing step.

Cure: The solidification of the resin component of a composite part, locking in the part's geometry.

Dam: A strip at the edge of a part to prevent the vacuum bag from pinching the edge of the part. It also functions to minimize resin bleed during cure.

Debulk: The period a prepreg laminate spends under the vacuum bag before heat is applied to cure the resin.

Fibers: One possible form of the reinforcement phase of a composite material. Most commonly glass, carbon, or polymer fibers.

Gelation: The point during the curing of a polymer resin when the polymer chains have cross-linked to such an extent that they form a continuous network throughout the material. Before gelation the resin is able to flow, whereas after gelation the resin's geometry is essentially locked in place.

Laminate: Prepreg plies that have been stacked together to produce the desired part thickness.

Matrix: The continuous phase of a composite material. This flows around the reinforcement phase, protecting it and binding it together.

Microstructure: The morphology of a material at a small scales. Although usage is not well standardized, in the context of FRP composites microstructure most often refers to the material's structure on the scale of plies and fiber tows down to the scale of individual fibers.

Out-time: The total time that a roll of prepreg has spent out of a freezer. Typically prepreg products will have specified limits for maximum out-times.

Ply: A single layer of prepreg

Prepreg: A raw material for producing composite parts consisting of a fabric of high-strength fibers preimpregnated with a partially cured polymer resin. **Prepreg process:** A manufacturing process for composite materials that involves draping a resinimpregnated fabric (a prepreg) onto a mold and subsequently curing the resin to produce a composite part.

Reinforcement: The discontinuous phase of a composite material. Typically in the form of fibers, flakes or particles, these are combined with a matrix to produce a composite material.

Resin: A raw material that is processed into a solid polymer. In composites this most often refers to a liquid resin that can be cured to produce a thermoset polymer, but it can also refer to a pelletized thermoplastic that can be processed by melting.

Satin weave: A textile weave. In contrast with a plain weave, where the yarns or fibers alternate passing under and over the yarns or fibers running perpendicularly to them, in a satin weave the yarns or fibers travelling in one direction pass over several perpendicular yarns before passing under one. A "5-harness satin" weave indicates the yarns or fibers pass over four yarns and then under one yarn.



Tool: A form that raw prepreg is laid onto to give a part its shape.

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xvii

Dedicated to Sandi, Violet, and David

and in memory of Stephen Gyabronka

1 Introduction

Today, advanced composite materials are replacing metals and other more traditional materials across a wide range of industries. They can offer a desirable combination of properties, including excellent resistance to fatigue and corrosion, efficient utilization of raw materials, a reduced need for fasteners, and a greater ability to optimize designs, but perhaps the most important advantages are their high strength-to-weight and stiffness-to-weight ratios. These make composite materials especially attractive to industries where lightweight structures are important, especially aerospace.

1.1 History

The first primary aircraft structure made from composite was an experimental Spitfire fuselage made in August 1940 and was made from "Gordon Aerolite", a flax reinforced phenolic composite developed in the UK to address a wartime shortage of aluminum [1]. Although early composite materials were able to compete with aluminum, it wasn't until the 1960s, when the production of carbon fibres was industrialized, that the era of "advanced composites" truly began [2], and composites began to show significant performance advantages over aluminum aerospace parts.

Early advanced composite structures were produced using a "wet layup" process, where fibres were impregnated with resin and immediately placed onto a tool. To eliminate the need for part manufacturers to mix and handle wet resin, the prepreg process was developed in the late 1960s, where a fabric made from high-strength fibers is pre-impregnated with a partially cured resin. These prepreg materials are easier to handle and provide better control over the amounts of reinforcement and resin in the composite parts. By 1974 Boeing was using prepregs to produce entirely composite floor panels for the 747 [1].

One difficulty that has limited the use of composite parts - and continues to do so today - is the formation of voids during processing. The presence of voids can have detrimental effects on the

material, such as reducing its compressive and shear strengths, transverse tensile strength, and fatigue resistance [3].

For many composite parts the formation of voids is currently suppressed by the use of an autoclave cure. By pressurizing the autoclave during the cure, typically to around 600 kPa (6 atmospheres) of pressure, voids are compressed and gas is driven into solution in the resin [4] [5]. Although this is a robust method of producing high quality parts it is also an expensive in terms of capital, energy, and time [6] and there is much effort current being spent to develop the capability to produce equivalent quality parts without an autoclave, known as out-of-autoclave ("OOA") processing. The development of a robust OOA process would have many benefits:

- Eliminate the cost of the autoclave, which can reach hundreds of millions of dollars in the case of large aerospace parts.
- Increase production speeds by eliminating the bottleneck of the autoclave.
- Open up the use of composite materials to smaller fabricators and low-cost parts, where the expense of an autoclave can't be economically justified.

A scientific understanding of the void phenomenon has long been seen as the key to developing a robust manufacturing process using OOA prepreg [7], and could also expand the range of parts that can be manufactured by autoclave processes as well.

1.2 Processing of Prepregs

Prepreg is the raw material for the prepreg process. It consists of thin sheets, typically a fraction of a millimeter thick, and is commercially available in rolls of various widths. Prepreg consists of two phases. The first phase is a high-performance fibre reinforcement, typically carbon fiber, glass fiber, or a polymer fiber such as aramid. This fiber reinforcement is typically in the form of a woven or unidirectional fabric. The second phase is a partially cured or "b-stage" polymer resin film that has been

partly or fully impregnated into the fabric phase. In some contexts prepreg is conceptualized as consisting of three phases, with the third phase being any voids not filled by the fiber or resin. A macrophotograph of typical prepreg is shown in Figure 1.1. The black material is a woven carbon fiber fabric having a 5-harness satin textile weave. In this prepreg the resin film is applied to the opposite side, but it can be seen as shiny spots where it has flowed through the fabric. The plastic film at the left of Figure 1.1 is a protective covering that is removed during processing.



Figure 1.1: Macro-photograph of prepreg

There is enormous variety in the prepreg available commercially. Most significantly, they can vary in the type of fibers they contain, the textile weave of the fibers, the number of fibers in each tow, the type of resin, the quantity of resin present, and the location and arrangement of the resin.

Prepreg that is optimized for use out-of-autoclave is typically different from prepreg intended for autoclave use in several ways. OOA prepregs are typically the partially impregnated or "breathable" type, as this leaves an interconnected network of voids within the material that is able to act as gas channels. These channels are known as engineered vacuum channels or "EVaC's". EVaC's are important in adding breathability to the material which allows a vacuum system to extract as much gas as possible during processing. OOA prepreg is also formulated with a resin system that has a high viscosity at room temperature, but a low viscosity at elevated temperatures. This helps the EVaC's to remain open under the vacuum bag while at room temperature but allows the resin to quickly and completely flow into the EVaC's when exposed to elevated temperatures during the cure cycle. Finally, OOA prepregs typically use resin systems that do not generate volatiles as reaction by-products, and are impregnated into the reinforcement using a hot-melt, rather than a solvent-bases method, to minimize the content of dissolved volatiles in the resin.

The process of manufacturing a part from prepreg consists of several steps that each play an important role in transforming the raw prepreg material to a finished part (see Figure 1.2).



Figure 1.2: Schematic of the Prepreg Process

Raw Material: The raw material for the prepreg process is a commercially available product typically available in a sheet form on wide rolls or in a tape form on narrow reels. Prepreg raw material is kept at low temperature during shipping and are stored in a freezer until it is ready to be used in order to slow the curing of the resin. It is also stored along with a desiccant inside a bag, usually polyethylene, which acts as a moisture barrier. Before use the roll of prepreg is removed from the freezer and allowed to warm to room temperature before it is removed from the bag. Next the prepreg is unspooled from the roll and cut into plies of appropriate shape and size for the part being produced.

Layup: In the layup step the paper or plastic backing is removed from the prepreg plies, exposing a tacky epoxy surface. The plies are then placed onto a tool which gives the part its shape. The tool must be coated with a release agent ahead of time so the part will not bond to the tool during processing.

Debulk: After the layup step a vacuum bag is placed over the part and a vacuum is drawn under the bag. The time that the part spends under the vacuum bag before the cure step begins is called the debulk time.

Cure: The part, along with the tool and vacuum bag, are placed into an oven and heated according to a temperature profile which is typically specified by the prepreg manufacturer. The resin then cures and the geometry of the part becomes locked in. Often a second heating cycle known as a post-cure is necessary to achieve optimum mechanical properties.

Finished Part: Once the part has cured, the vacuum bag is removed and the part is separated from the tool. The prepreg process is complete, and the part can continue to secondary processing if necessary.

In the ideal case, all the gas contained in the material is removed by the vacuum system during the debulk and cure phases of the process, and the resin is able to flow into and eliminate all void space present in the part. In practice, however, there are several different reasons why the final part could contain voids. These are summarized in figure 1.3.

5



Figure 1.3: Sources of voids in the prepreg process

One common framework for thinking about void formation in prepregs is the "sources and sinks" paradigm, where mitigating voids is thought of as balancing mechanisms that generate voids, or "void sources", with mechanisms that remove voids or "void sinks" [8]. In this framework air trapped between plies, air initially present within plies, vaporization of moisture and other volatiles, and incomplete resin infiltration can be seen as void sources. In OOA processing the only void sink available to us is the exsuction of gasses and volatiles by the vacuum system. In autoclave processing the autoclave pressure can be thought of as an additional void sink, and the absence of this void sink can be thought of as the principal difficulty in producing fully dense parts using an OOA process.

Figure 1.4 shows cross-sectional micrographs of typical composite parts made using the OOA prepreg process.



Figure 1.4: Typical prepreg microstructure

The voids of concern in parts made using the prepreg process are microstructural features with dimensions ranging from the scale of individual fibers (around ten microns) up to the scale of fiber tows (several millimeters). Voids larger than this are not usually seen unless there is a significant error made during processing. Voids are often classified according to their locations [9] as shown in Figure 1.5.



Figure 1.5: Taxonomy of voids

Surface voids appear as a discontinuity in the smooth surface of a part. They are not usually detrimental to the structure of a part, but are undesirable because they are aesthetically unpleasing and can affect the part's aerodynamics. Surface voids are not taken to contribute to the bulk porosity of a part. Conversely, internal voids are located in the interior of a part and do have a detrimental effect on mechanical properties. For every one percent increase in bulk porosity a composite material experiences a reduction in mechanical properties such as shear strength and stiffness, compressive strength, and transverse tensile strength of up to 10% [3]. The allowed porosity level in aerospace components is typically set at 1% to 2% [8]. Internal voids are often further classified as fiber tow voids, resin voids, and interlaminar voids. Fiber tow voids are small voids that are located within the fiber bundles themselves. Resin voids are larger voids that are located in between plies of material. Fiber tow voids are usually the smallest type and are often referred to as *microvoids*, whereas the term *macrovoids* refers to voids located outside the fiber tows.

Porosity is one of the main reasons for rework, repair and scrapped parts in the aerospace industry and the scientific fundamentals have never been fully understood. The reasons why the void phenomenon has been difficult to solve was articulated well in 1986 by Kardos, Duduković and Dave in one of the early publications to discuss the problem:

> "Clearly, the void phenomenon occurs during a very complex fabrication process involving heat, mass; and momentum transfer with simultaneous chemical reaction in a multiphase system with time-dependent material properties and boundary conditions. To model such a process by using first principles of transport phenomena is clearly difficult, and solution of the complex differential equations in closed form is not tenable."

> > -Kardos et al., 1986 [7]

Nearly 30 years later, the void phenomenon remains without a robust scientific understanding. Manufacturers must carry out an expensive and time-consuming process development project when they wish to produce a new part [10], because there is currently little to no predictive capability available to assist in designing a process that will be able to produce a void-free part.

2 Literature Review

Most of the research investigating the phenomenon of porosity in prepreg composites has its roots in work done in the 1980s by Kardos et. al [7] and by Loos and Springer [11] who considered composite processing from the point of view of interacting transport phenomena and related these to factors like temperature, pressure and moisture content. The link between void formation and volatiles was identified, and moisture was identified as an important volatile. Models involving flow of one or more phases were suggested [12] [11]. The relationship between the pressure applied to the vacuum bag, and resin pressure and the load carried by the fiber bed was discussed by Campbell et. al [13]. A clearer understanding of the role of vacuum bags was also provided by Thompson [14].

Most of the early work was in the context of autoclave processing, but industrial work beginning around 2000 led to the development of prepregs optimized for cure out-of-autoclave. As much of this work was in a commercial context the details of the development of these materials was proprietary and was not well documented publicly, but more recently university researchers have taken on the task of building a fundamental understanding these materials. This effort has led to enormous progress recently in understanding and modelling the processing and behavior of prepregs.

2.1 Physical Mechanisms

There are several important physical mechanisms that occur simultaneously during the debulk and cure steps of the prepreg process. These mechanisms and their and interrelationships determine the final microstructure of the part produced, including the porosity level. Previous literature has focused on some of the mechanisms that we expect to be important in prepreg processing, but has also ignored some of these. Here we summarize the work in the field to date and identify several important mechanisms that previous literature has largely neglected.

10

2.1.1 Gas Flow

Particularly in OOA prepreg processing the successful removal of gasses and dissolved volatiles depends on the transport of these through interconnected channels in the material, and accordingly much work has focused on understanding these gas transport processes. During the debulk phase the part is placed under a vacuum bag and a vacuum pump is connected. The vacuum pump creates a pressure difference



between the gas within the channels and the gas at the edge of the part. This causes the gas in the channels to be drawn toward the vacuum system.

Somewhat counter-intuitively it was found that prepreg with greater initial porosity could produce lower porosity parts because the greater breathability allowed gas transport to occur more easily [15] [16]. Flow through the thickness of the part was differentiated from in-plane flow [17] [18], and considerable research effort has been devoted to the measurement of the gas permeability of various OOA prepregs [19] [20] [21]. Based on this, models for vacuum evacuation have been proposed [8]. The permeability of these gas pathways is closely related to the degree of resin impregnation, as the gas pathways must remain open for gas evacuation to occur [22].

The details of this gas flow will depend on the structure of the prepreg being used and the vacuum bagging arrangement. In many prepregs (including MTM45-1/5HS, the prepreg that is the focus of this thesis) the resin is in the form of a film between the layers of fabric. This arrangement can prevent gas from easily travelling through the thickness of the part (Figure 2.2), and the permeability in the through-thickness direction will be lower than the in-plane permeability [23], often by 4 or 5 orders of magnitude.

11



Figure 2.2: Initial prepreg microstructure

In these materials the flow of gas through the thickness of the material will be minimal and most gas transport will occur in-plane. This will also be the case for any prepreg that is vacuum bagged with a non-permeable release film, as this will also tend to prevent gas transport in the thickness direction. In certain prepreg products (for example Cytec Solvay's "Z-preg" products) the resin film is applied in stripes leaving gaps of dry fabric between the strips so that gas can travel more easily in the thickness direction [24]. These prepregs are also used with a vacuum bagging arrangement that allows the vacuum system to access the top surface of the laminate.

The flow of gas through the vacuum channels within prepreg have typically been described using Darcy's law [8] [19]. Darcy's law was originally developed in the field of hydrology as an empirical relationship to describe the motion of water through soil, although it was later derived from the Navier-Stokes equations as well. It states that the velocity of a fluid through a porous medium is inversely proportional

to the fluid's viscosity, and directly proportional to the pressure gradient and to the medium's permeability, an empirically determined property of the medium.

Darcy's law in one dimension can be expressed as:

$$v = -\frac{K}{\mu}\frac{dP}{dx} \tag{1}$$

where v is the superficial fluid velocity, μ is fluid viscosity, and dP/dx is the pressure gradient. Note that superficial velocity is equivalent to volumetric flow rate (Q) per unit of cross sectional area (A):

$$v = \frac{Q}{A}$$
(2)

Some typical values found in the literature for permeability of prepregs are shown in Table 2.1.

Author	Value (m ²)	Comments
Farhang [9]	$1.56 \cdot 10^{-13}$	MTM45-1, Initial in-plane permeability during cure
Farhang	$2.63 \cdot 10^{-15}$	MTM45-1, Lowest measured nonzero in-plane permeability
		during cure
Hsiao [25]	$6.46 \cdot 10^{-14}$	5320/T650, highest permeability specimen, in-plane
Hsiao	$5.05 \cdot 10^{-14}$	5320/T650, lowest permeability specimen, in-plane
Hsiao	$1 \cdot 10^{-13}$	5320/T650, Initial in-plane permeability during debulk
Hsiao	$6 \cdot 10^{-14}$	5320/T650, Final in-plane permeability during debulk
Centea &	$1 \cdot 10^{-14}$	MTM45-1, in-plane
Grunenfelder		
[23]		
Centea &	$1 \cdot 10^{-18}$	MTM45-1, through thickness
Grunenfelder		
Louis [26]	$3 \cdot 10^{-14}$	MTM45-1, in plane
Louis	$6 \cdot 10^{-19}$	MTM45-1, 1 ply through thickness
Louis	$< 1 \cdot 10^{-20}$	MTM45-1, 2 plies through thickness

Table 2.1: Typical measured permeability values

Darcy's Law assumes laminar flow and so is expected to be valid when the permeability-based Reynolds number is less than 1. [27] In practice Darcy's law can be applied up to a Reynold's number of about 10, beyond which the relationship between velocity and pressure becomes nonlinear. [28] The permeability-based Reynolds number used for fluid flow through a porous medium is expressed in terms of density ρ , velocity v, permeability K, and viscosity μ [27]:

$$Re = \frac{\rho \cdot v \cdot \sqrt{K}}{\mu} \tag{3}$$

Value	Low Value	Condition	High Value	Condition
ρ	$1.3\cdot 10^{-6} kg/m^3$	Air density at limit of typical vacuum pump	1.3 <i>kg/m</i> ³	Ambient pressure
v	Approaching 0	Approached after long time under vacuum bag	0.02m/s	Darcy flow with pressure gradient of 1 atm/40mm
К	Approaching 0	End of cure cycle	$10^{-13}m^2$	Initial permeability of MTM45-1
μ	$1.3 \cdot 10^{-5} Pa \cdot s$	Water vapour	$1.85 \cdot 10^{-5} Pa \cdot s$	Dry air
Re	Approaching 0	-	10 ⁻³	-

 Table 2.2: Range of parameters for calculation of Reynolds number in gas flow

Over the range of parameters shown in Table 2.2 the permeability based Reynolds number of any gas flow we might plausibly encounter will always be less than 10^{-3} , and therefore gas flow through the EVaC's in prepreg is expected to always be laminar.

2.1.1.1 Klinkenberg Effect

To date the Klinkenberg effect has been largely ignored in the literature on gas transport in prepreg materials. Most authors have not considered it at all, and although Farhang [9] discusses the effect briefly she does not include it in her use of Darcy's law. Considering the pressures and permeability values encountered in OOA prepreg processing, however, it can be expected to be an important effect. The version of Darcy's law expressed in equation (1) requires that flow occurs in the viscous regime. In gasses this requires that the average distance that a gas molecule travels between collisions, or *mean free path,* is much smaller than the diameter of the channels the gas is flowing through. This is necessary because viscous effects in gasses are due to collisions between gas molecules which transfer momentum between fluid layers. At low pressures and in small channels this assumption is not valid because the collisions between gas molecules do not occur frequently enough to give rise to the phenomenon of viscosity at this scale. Because of this the no-slip condition at the boundary of a channel does not hold and the result is that the flow is faster than Darcy's law would predict.

The Knudsen number is a dimensionless number that compares the mean free path with the characteristic dimension of a channel:

$$Kn = \frac{\lambda}{l} \tag{4}$$

where λ is the mean free path and l is the characteristic length scale of the channel. When the Knudsen number is less than 1 the channel is larger than the mean free path, and Darcy's law is valid. When the Knudsen number is near or greater than 1 then Darcy's law must be modified.

The dimension of the EVaC's within a prepreg range greatly in size. The smallest are the voids known as *microvoids* - channels within a bundle of fibers - which have a characteristic dimension on the order of the diameter of the fibers themselves, around 5 microns $(5 \cdot 10^{-6}m)$ [29]. The largest gas pathways are the *macrovoids* - channels between the fiber bundles or between plies, which may have a characteristic dimension on the order of microns $(10^{-4}m)$.

The mean free path can be calculated using [30]:

$$\lambda = \sqrt{\frac{\pi}{8}} \cdot \frac{\mu}{u} \cdot \frac{1}{\sqrt{\rho \cdot P}}$$
(5)

where u is 0.4987445, and is dimensionless and P is gas pressure [30].

The range of values encountered in the problem of gas transport in prepreg laminates are:

Value	Low Value	Condition	High Value	Condition
μ	$1.3 \cdot 10^{-5} Pa \cdot s$	Water Vapour	$1.85 \cdot 10^{-5} Pa \cdot s$	Dry Air
ρ	$1.3 \cdot 10^{-6} \text{ kg/m}^3$	Air density at limit of typical vacuum pump	1.3 kg/m^3	Ambient
Р	0.1 <i>Pa</i>	Pressure at limit of typical vacuum pump	101300Pa	Ambient
λ	$4.5 \cdot 10^{-8}m$	-	$6.4 \cdot 10^{-2}m$	-

Table 2.3: Range of parameters for mean free path calculation

The range of values of the mean free path of air under this range of conditions is $4.5 \cdot 10^{-8}m$ to $6.4 \cdot 10^{-2}m$. This range spans the characteristic dimensions of EVaC's in prepregs, and therefore we expect to encounter both viscous and molecular flow in prepreg gas transport mechanisms.

In practice this effect is typically accounted for by modifying Darcy's law using the Klinkenberg correction [31]. Here the permeability K in equation (1) is replaced with a term that depends on the pressure:

$$K_{effective} = K\left(1 + \frac{b}{P}\right) \tag{6}$$

where K is the permeability measured using a liquid or, equivalently, a gas at sufficiently high pressure that the flow is in the viscous regime. Here b is called the Klinkenberg parameter and has dimension of pressure. The Klinkenberg parameter is usually determined from empirical relationships such as [32]:

$$b = 0.112Pa \cdot \left(\frac{K}{1m^2}\right)^{-0.39}$$
(7)

Typical in-plane gas permeability values for prepregs are [23] on the order of $10^{-14}m^2$, giving a value for b on the order of 30 kPa. The prepreg used in the experiments described in this work is MTM45-1 5HS which has a relatively high gas permeability, sometimes measured as high as $1.5 \cdot 10^{-13}m^2$. This corresponds to a Klinkenberg parameter of around 11 kPa. The Klinkenberg effect will be most important when the gas pressure is less than b, and pressures well below this level are easily encountered during prepreg processing. Late in the debulk phase of prepreg processing, when most air has been removed, the main mechanism occurring is the removal of vaporizing moisture. Pressures at this stage are less than the vapour pressure of water (around 3kPa at room temperature) and so the Klinkenberg correction term may often represent an increase in the effective permeability of more than an order of magnitude.

2.1.2 Sorption of Volatiles

As gas is removed from the vacuum channels the pressure within them is reduced. The reduced partial pressures of any volatile substances disturbs the equilibrium between its concentration in solution in the resin and its vapour pressure in the vacuum channels. This causes volatiles to come out of solution and to vaporize into the channels. This occurs first by the



Figure 2.3: Desorption of volatiles

diffusion of volatiles through the resin toward the vacuum channels, and then by the vapourization of those volatiles at the interface between the vacuum channels and the resin. Over a sufficiently long debulk this has the effect of removing the volatiles from the resin. Consideration of absorbed volatiles is usually restricted to the resin because the absorption of volatiles in carbon fibers is negligible [33]. During the cure processing step the elevated temperatures will tend to cause any remaining volatiles in solution in the resin to vapourize, which can cause the growth of voids. In autoclave processes gasses and vapours can be caused to remain in solution or even to re-dissolve by the application of high pressures during the cure, but in OOA processes these vapours must flow through the void network and be removed by the vacuum system in order to produce low porosity parts. Some recent work has begun to focus on understanding the influence of resin pressure on void formation and growth. Several authors have investigated the effect of reduced ambient pressure on porosity and resin infiltration [34] [35]. Although it is difficult to measure resin pressure in-situ without also affecting the flow of the resin, some experiments have been carried out using microelectronic pressure sensors to attempt to directly measure pressure within the laminate [36] [37] [38].

The influence of volatiles dissolved in the resin has been a focus of some previous research efforts. Hsiao [39] investigated the sorption and desorption of moisture by prepregs. Several authors have worked on establishing the conditions under which dissolved volatiles can grow or can be prevented from growing [7] [40] [35]. In some resin systems there may be several volatiles present or even volatiles generated within the resin as by-products of the curing reaction itself; although, in OOA prepreg materials it has been established that moisture is usually the only significant volatile present [41]. For this reason consideration of volatiles in OOA prepregs is usually concerned only with the case of dissolved moisture. Models for the rate of void growth exist for idealized cases such as isolated voids in infinite resin, however, these models are not currently useful for modelling void growth in real prepregs [35].

During the debulk and cure steps when the moisture is removed by the vacuum system diffusion is the mechanism that transports moisture from deep within the resin to the interface between the resin and the internal network of gas channels.

18
Diffusion can be described by Fick's law:

$$J = -D\frac{\partial\phi}{\partial x} \tag{8}$$

where J is the diffusion flux, D is the diffusivilty, and $\frac{\partial \phi}{\partial x}$ is the concentration gradient.

Although diffusion has been considered in the context of the growth of isolated voids, it has been ignored in much recent work on prepreg. Unfortunately this has largely been based on a mistake that has been repeated through the literature. The original error occurs in Sequeira-Tavares et al. [21] where the authors justify ignoring diffusion by stating that the diffusion length associated with typical gasses over the time of a cure cycle is much less than the thickness of a typical composite part and thus can be neglected. Later work has cited this paper as justification to ignore diffusion when considering transport phenomena operating within prepregs, [26] [42] [25].

The original statement made in [21] is that the length scales on which Fickian diffusion operates can be approximately given by $2\sqrt{D \cdot t}$ where D is the diffusion coefficient and t is time. It is then stated that diffusion coefficients measured in the literature range up to a maximum of around $10^{-9}m^2/s$, and that this corresponds to a diffusion length of 0.8mm over a typical cure cycle of 5 hours. Unfortunately this value is incorrect, and is off by one order of magnitude; the correct diffusion length should be 8mm, which is not smaller than the thickness of a typical composite part.

Additionally, even if this figure had been correct the comparison with a typical laminate thicknesses is not necessarily appropriate. While 0.8mm is indeed less than the thickness of a typical laminate, during vacuum evacuation the moisture within the part does not diffuse through the entire thickness of the laminate, but rather diffuses only to the nearest vacuum channel where it vapourizes and is subsequently removed by gas flow to the vacuum system. These vacuum channels are present in each ply, and therefore diffusion occurs over half a ply thickness or less, a distance of around 0.05mm to 0.18mm depending on the prepreg. Diffusion is therefore expected to be an important consideration in the transport mechanisms governing void evolution in prepreg processing.

2.1.3 **Resin Flow**

As gas is removed from the gas channels and the pressure in the void space drops the resin may also begin to flow into the void space previous occupied by gas. In OOA prepregs the resin is typically formulated to have high viscosity at room temperature. This is done to prevent cold flow (the flow of resin at room temperature during the debulk processing Figure 2.4: Resin flow



step) as this could close off the vacuum channels prematurely, preventing further gas evacuation [22].

Like gas flow, resin flow in prepregs is typically modelled using Darcy's law, and there have been models based on Darcy's law proposed for the impregnation of tows by resin [43]. The permeability values for resin flow are different from the permeability values for gas flow because the flow occurs in a different direction and through different regions of the microstructure. The resin flows into the fiber bed during processing, whereas the channels that gas flows through can be located within the fiber bed, within resin regions, or between plies. If the flow of a planar resin film into a planar fiber bed layer is being considered, the permeability is in the through-thickness direction. Often the flow of resin into a single fiber bundle is considered [43], in which case the permeability is the radial permeability of the fiber tow. (See Figure 2.5.)





Radial resin flow

Linear resin flow

Figure 2.5: Resin Flow

Additionally, unlike gas flow there is no Klinkenberg effect because the resin is a liquid.

Table 2.4 shows the range of values plausibly encountered during resin flow in prepregs. The greatest Reynolds number plausibly encountered in resin flow is on the order of 10^{-10} , and therefore the flow will always be laminar and the use of Darcy's law for resin flow is justified.

Value	Low Value	Condition	High Value	Condition
ρ	1150kg/m ³	Uncured resin density	1180kg/m ³	Cured resin density
v	Approaching 0	Resin infiltration complete	$8\cdot 10^{-6}m/s$	Darcy flow with pressure gradient of 1 atm/ply
К	$10^{-15}m^2$	Measured transverse permeability*	$10^{-13}m^2$	Theoretical transverse permeability*
μ	3.5Pa · s [44]	Room temperature	23400Pa · s	Minimum viscosity encountered during cure [45]
Re	Approaching 0	-	10 ⁻¹⁰	-

Table 2.4: Range of parameters for calculation of Reynolds number of resin flow

* Typical transverse permeability measured is lower than theoretical by as much as 2 orders of magnitude [43].

2.2 Porosity Prediction

The possibility of predicting porosity from material properties and process parameters is of great interest to industry, and this possibility has been investigated. This type of approach was hinted at as early as the 1980s. For example, Loos and Springer [11] attempted to build a model through the coupling of sub-models representing the most important phenomena (although they consider a very different prepreg process than is considered here: an autoclave cure with resin bleed and no in-plane gas transport, and without a debulk step.) Their focus was on predicting thermal and chemical properties as well as resin flow and stress. They do consider porosity in their model, but admitted that modeling porosity required information that was not available and did not attempt to validate the use of their model to predict porosity.

More recent work on OOA prepregs has continued to seek predictive models for porosity, but success in this area has been somewhat limited. A principal reason why porosity prediction has been difficult appears to be variability. Several authors have performed experiments varying process parameters and measuring the influence on porosity [20] [46], and it has been noted that there is substantial variability in the experimental results. Variations in the initial raw material, such as resin content, resin moisture content, degree of impregnation, and permeability have also been shown. This variability can be between different rolls of nominally identical material, or even between different regions of the same material roll. Centea et al [47] [48] mention variability in fiber packing arrangements and transverse permeability. Grunenfelder et al [49] observed variations in tow impregnation and attribute this to variations in initial degree of impregnation, fiber packing, and permeability. Shim and Seferis [50] noted that "irregular resin coverage" is "usually found" in prepreg systems, attributed inconsistent air permeability results to this, and commented that this should be reduced to improve quality control. Farhang [9] used two different rolls of nominally identical MTM45-1/5HS material, and noted that the rolls differed in "initial ply thickness, porosity, surface morphology and permeability", with the

22

permeability differing by a factor of 5 between the two rolls. This variability has made porosity prediction very difficult, as even relatively small variations in these parameters can often have a large influence on porosity levels [51]. This variability means that two parts of identical size and shape can be made from the same prepreg product using the same process and can nonetheless have rather different porosity levels. Clearly deterministic models can only predict the porosity of cured parts to the extent that the experimentally measured porosity of cured parts agree with each other.

Although much work has been done to understand the evolution of porosity in prepregs by investigating the transport mechanisms operating during prepreg processing, the mechanisms have been considered in isolation. The novelty of this work is to look at the interactions of these mechanisms. Some additional references are included in Chapter 4 where the interactions between these transport mechanisms will be discussed and the times scales that these mechanisms operate over are considered.

3 Objectives

3.1 Objectives and Goals

The objectives of the present research are:

- To develop a <u>better scientific understanding</u> of the relationship between the porosity of cured parts and the parameters relevant to prepreg processing, with a focus on out-of-autoclave processing.
- To develop a <u>basic capability for predicting the porosity</u> that a part is expected to have given these relevant parameters, and to establish a framework that can be built upon to move toward improved models in the future.

The ability to predict the approximate porosity of parts from the process parameters is intended to benefit engineers by:

- Aiding in the design of new manufacturing processes, so process parameters can be chosen such that the parts produced are expected to have acceptably low porosity levels.
- Aiding in the troubleshooting of existing manufacturing processes where porosity has been a problem.

3.2 Tasks

Currently we understand some of the important mechanisms involved in processing prepreg, but are not able to use this understanding to make accurate predictions of the porosity levels that finished parts will have. To develop this ability will require an improved understanding of many of the mechanisms involved in prepreg processing, as well as an understanding of how they interact. To develop this understanding the author will:

- Propose a framework for understanding the most important mechanisms governing the evolution of voids during prepreg processing.
- Conduct experiments to measure the quantity of moisture absorbed by prepreg under various conditions.
- Investigate and quantify the extent of variability in the raw material.
- Experimentally measure the effect of varying process variables on bulk and surface porosity levels in cured parts.
- Construct a numerical model to simulate the action and interaction of the most important mechanisms that occur in prepreg during the debulk processing step.
- Attempt to estimate the porosity levels in cured parts from the outputs using this model.
- Evaluate the model's usefulness by comparison with experimentally measured porosity data.

The work presented here is particularly focused on the out-of-autoclave prepreg process because problems with voids are common in these processes. The experimental work is conducted on Cytec Solvay Group's MTM 45-1/5HS prepreg¹, a net-resin one-side-tacky in-plane breathing carbon-epoxy OOA prepreg. This material was chosen to provide continuity with the large body of experimental work performed on this material. It is also a good example of a typical OOA prepreg; this material has been used to produce some of the largest composite aerospace parts produced without an autoclave, including the *SpaceShipTwo* suborbital spaceplane that Virgin Galactic intends to use for space tourism and its carrier airplane *White Knight 2* [52].

¹ MTM45-1 was initially developed by British Company Advanced Composited Group or ACG. ACG's plant was purchased by Umeco in 2006 and subsequently by Cytec in 2012. Cytec was then acquired by Solvay in 2015.

4 Transport Mechanisms Framework: Interaction and Time Scales

The current state of the literature shows that the prepreg process involves several important transport mechanisms. Some of these are clear and well understood, and some have been ignored or are only partially understood. Additionally, attempts to model these mechanisms have done so only for single mechanisms in isolation, without attempting to couple them together.

The central idea of this thesis is that these transport mechanisms, which occur simultaneously and are interacting, are the most important mechanisms determining the evolution of the prepreg microstructure during processing, and that understanding the action and interaction of these mechanisms is the key to understanding and modelling the evolution of voids in OOA prepregs.

Here we will introduce a simplified model of prepreg microstructure that approximates the microstructure of real prepreg. Then we will establish the action of the transport mechanisms in the context of the simplified model. This *transport mechanisms framework* gives us an approximate picture of what occurs during prepreg processing, and it is hoped that this framework will act as an *intuition pump* [53] to aid in thinking and reasoning about prepreg processing. It is also hoped that it will serve as a starting point for the development of improved models in the future. We will also establish approximate time scales for these transport mechanisms based on the relevant process parameters.

4.1 Simplified Microstructure Model

Our simplified prepreg microstructure model is shown below in Figure 4.1. In the simplified model the prepreg consists of two regions, a *porous region* and a *nonporous region*. The porous region consists of the fiber bed and the interstitial space within the fiber bed, including all the voids and any resin that flows in to displace the voids. The non-porous region contains only resin and can be thought of as a reservoir of resin, ready to flow into the porous region.

26



Figure 4.1: Real and Simplified Prepreg Microstructure

As resin infiltration proceeds during processing the resin flows into the interstitial space in the fiber bed to displace the voids. In the ideal case where resin infiltration proceeds to completion and all voids are eliminated the final microstructure consists of a porous region fully infiltrated with resin and a nonporous region containing only a small balance of excess resin (see Figure 4.2). The case where voids remain in the final cured microstructure is equivalent to partial resin infiltration as the resin has not been able to displace all the voids.





Table 4.1 summarizes the differences between real prepreg microstructure and the simplified prepreg microstructure model.

Table 4.1: Comparison of real prepreg with	h simplified microstructure model
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Real Prepreg	Simplified Model
Fibers, resin & voids are in a complicated, non-uniform, somewhat random arrangement	Uniform layers of resin alternate with layers of fibers/voids
Fiber bundles are not straight and run in multiple directions	Fiber bed is homogeneous
Voids appear within resin, between layers, or within fiber bundles	Physical arrangement of voids is ignored
Details of resin infiltration is complicated, different types of voids fill at different rates as resin flows through and around fibers	Resin displaces void space as resin infiltration proceeds, but details of this flow is ignored
Most voids form an interconnected network, but a small fraction of the voids may be isolated ("resin voids")	All voids form a interconnected network of gas channels

Our simplified model dispenses with many features of real prepreg to achieve an approximate model that is useful for conceptualizing what occurs during processing of prepreg. The important features of the system are only that resin, fibers and voids are all present, gas can flow through the interconnected material, resin can flow into and displace the void space, and the fibers do not move.

4.2 Interaction of Transport Mechanisms

We can now add the transport mechanisms to our simplified microstructure model. To successfully

produce parts with low porosity levels, these processes must act to:

- Allow the vacuum system to remove gas from the interconnected network of gas channels.
- Remove dissolved moisture from the resin by causing it to diffuse toward the gas channels, vapourize, and then flow through the gas channels to the vacuum system.
- Infiltrate the now evacuated void spaces with resin to eliminate void space from the part.
- Cure the resin to produce a composite part.

The principal transport mechanisms involved in void evolution in prepreg processing are the flow of gas through (and out of) the prepreg, moisture sorption at the interface between the resin and the vacuum channels, moisture diffusion through the resin, and the flow of resin into the void space. The action of these mechanisms is shown schematically in the context of a single ply of prepreg in Figure 4.3.



Figure 4.3: Physical mechanisms operating during OOA prepreg processing

At the end of the layup step the material is in the form of layers of prepreg applied to a tool. The reinforcement fibers are not fully impregnated with resin, and so they contain gas-filled channels. These gas-filled channels form an interconnected network which gives the material a high permeability in the plane of the layers.

In the debulk step the part is placed under a vacuum bag at room temperature. Gas within the channels flows through the material to the vacuum system. Moisture dissolved in the resin diffuses toward the channels and vaporizes, representing a source of additional gas that must be removed by the vacuum system. Although the resin viscosity is very high, the resin is slowly drawn toward the channels by the low pressures within them.

After some time under vacuum (the "debulk time") the temperature is increased to begin the cure step. As the temperature rises the viscosity of the resin decreases by several orders of magnitude and the resin is quickly drawn into the void spaces. The elevated temperatures also allow a chemical reaction to proceed in the resin which releases additional heat, and has the effect of hardening the resin, binding the reinforcement phase together. The curing reaction has the effect of increasing the viscosity of the resin, so the resin viscosity reaches a minimum value and then increases. Eventually the curing of the resin reaches the point of gelation where an elastic modulus develops. Beyond this point the resin is no longer capable of fluid-like flow and the part's microstructure is essentially locked in. The elevated temperature during the cure also increases the vapour pressure of any dissolved moisture remaining in the resin, which can cause voids to grow if the resin has a high moisture content.



Figure 4.4: Interaction of transport mechanisms

The interaction between these mechanisms is shown in Figure 4.4. The coupling between these transport mechanisms can be most easily seen by considering how dissolved moisture is removed from the resin. The mechanisms of diffusion, sorption, and gas flow are a "chain" of transport mechanisms that act in series to remove moisture in several steps. The driving force for diffusion of moisture in the resin is the gradient in moisture concentration between the bulk resin and the resin at the surface of the gas channels. The driving force for the sorption mechanism is the difference in the vapour pressure

between this surface resin and the gas in the adjacent gas channels. Finally, this vapour pressure is one component of the gas pressure in the gas channels, which is one end of the pressure gradient driving gas flow to the vacuum system. Finally, the difference between this local gas pressure and the far-field resin pressure is the driving force for the flow of resin into the fiber bed.

4.3 Establishing Approximate Time Scales

The transport mechanisms summarized above operate over time scales that depend, in general, on the geometry of the part, the arrangement of the vacuum system, and on the material properties of the prepreg and its constituents. Looking at the time scales that these mechanisms operate over is important for understanding the interaction between these transport mechanisms. For example, the removal of gasses from within the material occurs by flow through the vacuum channels, and this depends on those channels remaining open. The infiltration of resin into the void space closes these channels, and so the time scale for the gas flow mechanisms must be shorter than the time scale for resin infiltration. By looking at the time scales we can also see if one mechanism will be dominant. For instance, if one mechanism operates on much shorter time scales than other mechanisms that it acts in series with it can often be ignored.

4.3.1 Time Scale for Dry Gas Flow

An approximate time scale for Darcy's law can be obtained from the nondimensionalized version of Darcy's law (See Appendix A). This time scale is:

$$t_{Gas\,Flow} = \frac{\phi \cdot \mu \cdot L^2}{K \cdot P_0} \tag{9}$$

where ϕ is porosity, μ is gas viscosity, L is breathe-out distance, K is permeability and P_0 is the initial pressure. Typical values in prepregs are $\phi = 0.35$, $\mu = 1.85 \cdot 10^{-5} Pa \cdot s$, $P_0 = 101300 Pa$. The range of in-plane gas permeability for prepregs found in the literature is $10^{-15}m^2$ to $10^{-12}m^2$, but especially for OOA prepregs values in the range of $8.5 \cdot 10^{-15}m^2$ to $1.5 \cdot 10^{-13}m^2$ are typical.

Note that equation (9) assumes no Klinkenberg effect. For dry gasses this is a reasonable omission because the dry gasses are removed quickly during the early part of the debulk step, and most dry gas is removed before low enough pressures are encountered for the Klinkenberg effect to become important.

Assuming Darcy's law in 1D, uniform initial pressure, and a step change in pressure at one boundary, the time for the mass change to get 90% of the way to an equilibrium state is about 6 time constants (See appendix A). Using this criterion, we can plot the range of time scales for the flow of dry gas out of a laminate over the range of permeability and length scale values typically seen in OOA prepreg processing. This is plotted along with the time scales for diffusion and gas transport of moisture in Figure 4.5. The range represents the typical range of permeability values for OOA prepregs, and the dashed line represents a permeability value at the geometric mean of the range, about $3.6 \cdot 10^{-14} m^2$.

4.3.2 Time Scale for Moisture Vapour Flow

When vapourizing moisture is being removed from the part in the latter part of the debulk the situation is similar to the removal of the dry atmospheric gasses but the driving pressure is much lower in this stage and the Klinkenberg effect is important. During most of the debulk step only the vapour pressure of the absorbed water is available to drive the flow of moisture vapour vapour through the gas channels to the vacuum system. This driving pressure will depend strongly on temperature and so the time scale for moisture vapour flow will depend strongly on temperature as well. The vapour pressure of water can be calculated from the Antoine equation [54]:

$$P_{H2O}^{*} = \frac{101300}{760} \cdot 10^{\wedge} \left(8.07131 - \frac{1730.63}{233.426 + T_{celsius}} \right)$$
(10)

The vapour pressure of the absorbed moisture will be somewhat less than the vapour pressure of free water at the same temperature, but this will be adequate for the purposes of calculating time scales here. Here we will take the vapour pressure of the absorbed moisture to be 2.3 kPa.

To produce a rough estimate of the time scale involved in moisture vapour flow we use (9) but substitute the vapour pressure of the dissolved moisture for P_0 and apply the Klinkenberg correction term to the permeability K, assuming that same pressure, with the Klinkenberg parameter b calculated using (7).

$$t_{Moisture \,Vapour \,Flow} = \frac{\phi \cdot \mu_{H2O} \cdot L^2}{K \cdot \left(1 + \frac{b}{P_{H2O}}\right) \cdot P_{H2O}} = \frac{\phi \cdot \mu_{H2O} \cdot L^2}{K \cdot (P_{H2O} + b)} \tag{11}$$

As with dry gas flow we take 6 of these time constants as our time scale for moisture vapour flow. The range of time scales corresponding to 6 of these time constants is plotted in Figure 4.5 for parts of various length. The same range of permeability values are assumed here as for dry gas flow and the corresponding Klinkenberg parameters calculated using (7). A typical moisture content of 0.3% is assumed here, and the viscosity of water vapour is taken to be $\mu_{H20} = 9.90 \cdot 10^{-6} Pa \cdot s$.

4.3.3 Time Scale for Diffusion

The approximate time scales involved in Fick's law can be obtained from the nondimensionalized version of Fick's law (See Appendix B). This time scale for 1D diffusion (2-sided case is):

$$t_{Diffusion} = \frac{L^2}{4D} \tag{12}$$

The range of diffusion coefficients for moisture in uncured epoxy resins found in the literature ranges from $10^{-11}m^2/s$ to $10^{-9}m^2/s$ [21], whereas values for cured epoxies are typically around $10^{-13}m^2/s$ [55]. In prepregs the epoxy is partially cured and so the diffusion coefficient is expected to be intermediate between these values. Additionally, prepreg also contains impenetrable components in the form of fibers, and gas channels through which moisture diffuses relatively quickly. For this reason, the effective diffusion coefficient of a prepreg may be substantially different than the neat resin it contains, and could be either higher or lower. In the prepreg studied here, MTM45-1, the diffusion coefficient of moisture in neat resin is measured to be $2.6^{-12}m^2/s$ and there is some evidence that it can often be somewhat lower than this (see sections 9.4, 11.1). The effective diffusion coefficient measured for the as laid-up prepreg was around one order of magnitude greater than the value for the neat resin only. Here L is the length the diffusion is occurring over, which for moisture diffusion in OOA prepregs is on the order of half of one ply thickness.

Assuming Fick's law in 1D, uniform initial concentration, and a step change in concentration at one boundary, the time for the mass change to get 90% of the way to an equilibrium state is about 0.8 time constant. (See appendix B). Using this criterion, we find the time scale ranges from about 10 seconds to 12 minutes. Here we have used L=0.09mm which is half the resin film thickness in the MTM45-1/5HS prepreg studied in chapter 6. This time scale is plotted in Figure 4.5. The dotted line assumes the measured diffusion coefficient of MTM45-1, $2.6 \cdot 10^{-12} m^2/s$, and the range shown represents a factor of 2 greater and smaller than this value.



Figure 4.5: Time scales for moisture diffusion and flow of dry gas and moisture vapour. (Best in colour when available)

4.3.4 Time Scale for Resin Infiltration

The time required for a resin layer to completely infiltrate a fiber bed is given by:

$$t_{\text{infiltration}} = \frac{\phi_{\text{fiberbed}} \cdot \mu_l \cdot h_f^2}{2 \cdot K_l \cdot P_\infty}$$
(13)

Where $\phi_{fiber \, bed}$ is the porosity of just the porous region, μ_l is the resin viscosity, h_f is half the fiber bed thickness, K_l is the transverse permeability of the fiber bed, and P_{∞} is the compaction pressure. (See Appendix C for derivation). For the MTM45-1/5HS prepreg studied here the parameters are $h_f = 0.175 mm$, $K_l = 10^{-15} m^2$, $\phi_{fiber \, bed} = 0.46$. Compaction pressure is assumed to be $P_{\infty} = 1atm$.

The viscosity of the resin will primarily depend on temperature. The initial viscosity of the resin as a function of temperature for MTM45-1 resin is shown in Figure 4.6 [45].



Figure 4.6: Initial viscosity of MTM45-1 resin.

The data points shown in Figure 4.6 are generated by the software Raven 3.5.0 [45], which uses the NCAMP MTM45-1 model [56]. The curve shown is the following fit to the data:

$$\mu = exp(0.000338 \cdot T^2 - 0.132 \cdot T + 13.2) \tag{14}$$

with viscosity in Pascal seconds and temperature in degrees Celsius.

This approach assumes the resin viscosity remains constant during the entire debulk, but in reality the advance of the cure will increase the viscosity. A plot of MTM45-1 resin viscosity during constant temperatures debulks is shown for various temperatures in Figure 4.7.



This figure shows that at higher temperatures and longer debulk times the assumption of constant viscosity will not hold, but a reasonable model for the time at a given temperature before the viscosity begins to change substantially is given by:

$$t_{constant\ viscosity} = \frac{\mu}{1000\ Pa \cdot s/day} \tag{15}$$

where μ is the initial viscosity given by equation (14). The points corresponding to these times for each temperature are shown as black dots in Figure 4.7. The increase in viscosity before this time is less than 10% at all temperatures.

By solving (15) for μ , substituting this into (16) and rearranging:

$$\frac{t_{\text{inf iltration}}}{t_{\text{constant viscosity}}} = \frac{\phi_{\text{fiber bed}} \cdot 1000Pa \cdot s / day \cdot h_f^{-2}}{2 \cdot K_l \cdot P_{\infty}}$$
(16)

This is valid as long as the resin viscosity is approximately constant over the entire infiltration time. For the values listed above the right hand side evaluates to:

$$\frac{0.35 \cdot 1000 Pa \cdot s / day \cdot (0.175 mm)^2}{2 \cdot 10^{-15} m^2 \cdot 1atm} = 0.8$$
(17)

The resin infiltration time is therefore shorter than the time over which constant viscosity can be assumed, and so (24) is valid. For any constant temperature debulk resin the infiltration will be completed before the viscosity begins to increase substantially, and so this approach will provide a valid infiltration time for any constant temperature debulk. The time scale for resin infiltration is shown in Figure 4.8.



Figure 4.8: Time scale for resin infiltration

At room temperature even extremely long debulk times (on the order of several days) should see only modest resin flow, whereas at higher temperatures the resin infiltration can occur in less than one hour. At a temperature of 120°C, a typical curing temperature, resin infiltration would occur in less than 10 minutes.

If the time scale for resin infiltration needs to be estimated for a resin where the viscosity is not approximately constant during the resin infiltration a flow index approach can be used². This approach can also be used to estimate resin infiltration time scales in real cure cycles where viscosity is not constant because temperature is not constant.

² Flow index as defined in (18) is a useful concept that has been used within the UBC composites research group and in the Raven software produced by Convergent Manufacturing Technologies; however, the author was unable to find a reference to this concept in the existing composites literature.

Define the flow index as:

$$\int_{0}^{t} \frac{1}{\mu_{l}(t)} \cdot dt \tag{18}$$

The flow index corresponding to complete resin infiltration is given by:

$$\int_{0}^{t} \frac{1}{\mu_{l}(t)} \cdot dt = \frac{\phi_{fiber\,bed} \cdot h_{f}^{2}}{2 \cdot K_{l} \cdot \left(P_{\infty} - \sum P_{i}\right)} \tag{19}$$

(See Appendix C, section C.2 for derivation). This quantity can be determined using process simulation software. For example, Raven by Convergent Manufacturing Technologies automatically calculates the flow index for every cure cycle simulation [57].

The time scale for resin infiltration plays a central role in prepreg processing because it acts as a time limit for the other mechanisms to act. The transport of gas and moisture out of the material during debulk and cure depends on the gas channels remaining open, and so they must occur before resin infiltration goes to completion. For this reason it must be ensured that the time scales for the transport mechanisms shown in Figure 4.5 are shorter than the time scale for resin infiltration.

39

5 Experiments: Moisture Sorption

The presence of volatiles during the processing of prepreg laminates is known to be a significant factor that influences porosity in parts produced from prepreg. Volatiles can be present in the raw material, or can be produced as a product of a chemical reaction during the cure processing step.

Measures are taken to minimize the amount of volatiles present during processing as these can lead to void formation during the cure step of processing. For example, resins that use addition polymerization rather than condensation polymerization are selected [58], and resins are combined with the reinforcement using a hot-melt process rather than a solvent-based one [36]. These strategies can reduce the quantity of volatiles present; however, because moisture is always present in air it is inevitable that all prepreg will have some moisture content. Even if it were feasible to produce prepreg having zero moisture content, dry prepreg would absorb moisture from its environment during shipping, storage, ply cutting, and layup. It is known that moisture is usually the only significant volatile in commercially available prepregs intended for OOA processing [41].

It can be shown that the quantity of moisture present in a typical prepreg is quite substantial compared to the quantity of air present in the vacuum channels. During prepreg processing absorbed moisture represents an internal source of gas that must be removed by the vacuum system along with the entrapped air. Although prepreg typically has an initial moisture content of well under 1%, this potentially represents a much greater quantity of gas than the entrapped gases initially present in the voids. Moisture content is defined as weight or mass of absorbed water over dry weight or mass. It is often expressed as a percent.

$$MC = \frac{m_{h2o}}{m_{dry}} = \frac{m - m_{dry}}{m_{dry}} \quad \text{or} \quad \%MC = \frac{m_{h2o}}{m_{dry} \cdot 100} = \frac{m - m_{dry}}{m_{dry} \cdot 100}$$
(20)

The number of entrapped air molecules per unit volume initially in the prepreg is given by:

$$\frac{n_{air}}{V} = \phi \frac{P}{RT}$$
(21)

where ϕ is the initial porosity. For the prepreg studied in this work the initial porosity is about 0.3, so at room temperature this value is about 12.4mol/m³. The number of dissolved water molecules in prepreg is given by:

$$\frac{n_{H2O}}{V} = MC \cdot \frac{\rho_{prepreg}}{M_{H2O}}$$
(22)

where MC is the initial moisture content, and $\rho_{prepreg}$ is the density of the prepreg. The density of the prepreg studied in the current work is about 1200kg/m³. The number of molecules of entrapped air and absorbed moisture can be plotted as a function of prepreg moisture content (Figure 5.1). The range of initial moisture content for the prepreg used in experiments below is also shown, along with the equilibrium moisture content of prepreg exposed to 33% and 75% relative humidity environments.



Figure 5.1: Concentration of air and water molecules in prepreg

This figure shows that in most cases there are expected to be substantially more molecules of water than molecules of dry air in the initial prepreg. It should be noted that unlike entrapped air, it is not necessary to remove all the moisture from the resin to avoid porosity. Some quantity of moisture can remain in solution during the cure and so the resin moisture content does not have to be zero. Experiments have shown, however, that the moisture content of a prepreg can have a substantial influence on the porosity of parts produced in OOA processes [46].

5.1 Controlling Relative Humidity

Experiments were conducted by exposing either prepreg or neat resin to controlled relative humidity levels. This was achieved by placing them into sealed containers along with a humidity control medium. Several different humidity control media were used:

Humidity Control Medium	Humidity Level	Notes:
Silica-gel Desiccant	0%	
Saturated salt solution	Depends on salt chosen	NaCl - 75% relative humidity
	(See appendix D)	MgCl - 33% relative humidity
Water/Glycerine Solution	Selectable by glycerine	Greater concentrations of glycerine
	concentration	reduce the relative humidity

Table 2: Humidity Control Media

Control of the relative humidity in the containers by the method of saturated salt solutions is described in ASTM E104-02 [59], and data on salt solutions and humidity levels was drawn from Winston [60] and Rockland [61]. Control by water/glycerine solutions is described in ASTM D5032 [62].

The humidity conditioning apparatus consisted of a closed container partially filled with a humidity control medium. A rack made from stainless steel mesh is also present and is used to support the laminate above the humidity control medium (see Figure 5.2). Humidity levels were checked by measuring them with a Fisher Scientific model *CON4385* probe hygrometer.



Figure 5.2: Example of a humidity conditioning container

5.2 Moisture and Relative Humidity

An experiment was conducted to determine the relationship between equilibrium moisture content and relative humidity for coupons of MTM45-1/5HS prepreg at room temperature. Four coupons of prepreg were cut from adjacent regions of a roll of raw material. All four coupons were 64mm by 64mm, and 4 plies thick. These were placed in a container where the relative humidity was controlled by the use of a water/glycerine solution.

The prepreg coupons were first placed in a sealed container along with a silica-gel desiccant and allowed to equilibrate. They were then weighed, and this is taken as their dry weight. Next they were placed in a sealed container along with a water/glycerine solution and allowed to equilibrate with the atmosphere inside the container, typically taking three to five days. The weight was then measured again and the relative humidity was subsequently increased by adjusting the ratio of water to glycerine in the humidity control medium. This was repeated several times to determine the quantity of moisture absorbed by the coupons at different humidity levels. The moisture content can be calculated using:

$$MC_i = \frac{W_i - W_d}{W_d}$$
(23)

where MC_i is the initial moisture content, W_d is the dry weight, and W_i is the initial weight. The results are shown in figure 5.3.



Figure 5.3: Relationship between equilibrium moisture content and relative humidity at room temperature.

The agreement with a parabolic model proposed by Kardos et al. [7] is very good:

$$MC = k_1 \cdot (RH)^2 \tag{24}$$

Here a value of $k_1 = 0.00558$ is used, the value determined by Kardos et al. Although the original authors were studying an entirely different prepreg, the agreement with the current experimental data is remarkably good.

Different pieces of prepreg can be somewhat variable in the amount of moisture they will absorb, even for pieces cut from the same roll of material. This variability is more pronounced at higher relative humidity levels: at 100% relative humidity (not shown in Figure 5.3) the samples were sometimes observed to absorb moisture continuously without reaching equilibrium even after 40 days. The variation between samples also became extreme in this condition, with one reaching greater than 7% moisture content while another absorbed less than 1%. There is also some variability between different rolls of prepreg. For example, experiments performed on prepreg drawn from a different roll of the same prepreg product and had an average equilibrium moisture content of 0.26% at 75% relative humidity, lower than any of the coupons observed in this experiment.

5.3 Effect of Pressure on Equilibrium

Four single ply coupons of MTM45-1 were weighed and the placed in a container with a silica-gel desiccant. After allowing adequate time to equilibrate they were weighed again to establish a dry weight for each coupon.

Two coupons were then placed in containers along with a saturated NaCl solution to regulate the relative humidity at 75%. The other two coupons remained in the dry containers to act as controls. One of the humid containers was sealed, and remained at ambient temperature and pressure, while the other was placed in a rigid vacuum drum and pumped down to a gauge pressure of approximately -29.5 inHg.

Inside the vacuum drum the water vapour removed by the vacuum system is quickly replaced by evaporation from the salt water solution but the other atmospheric gasses are not replaced. Therefore the partial pressure of water vapour is the same in both containers, but in one container there are other atmospheric gasses present as well.

After allowing adequate time to equilibrate, the coupons were removed from their containers and weighed again. From this weight and the dry weight measured earlier the moisture content was determined, and is shown in Figure 5.4.

45



Figure 5.4: Effect of ambient pressure on moisture equilibrium

The coupon equilibrated at low pressure did not show a substantial difference from the ambient pressure coupon, and agreed almost exactly with the predictions of the parabolic sorption curve model. We conclude that the moisture equilibrium is affected only by the partial pressure of water vapour in the environment (ie. the relative humidity) and is negligibly influenced by the partial pressures of other gasses present.

5.4 Effect of Temperature on Equilibrium

To measure the effect of temperature on the equilibrium moisture content of prepreg, the experiment described in 5.2 was repeated at higher temperatures. An oven controlled by a digital temperature controller and thermocouple was used to regulate the temperature, and a dial hygrometer in the container was used to measure humidity levels. The temperature controller's set point was set to 40°C and 55°C, and the actual temperature within the humidity conditioning containers was measured at 41.6°C and 58.5°C respectively. Coupons were allowed adequate time to equilibrate with the atmosphere in the container and were then weighed to determine their moisture content. Water was

then added to the water/glycerine solution to increase the humidity level, and the process was repeated.

Equilibrium Moisture Content (%) 0.9 25<u>°</u>C 0.8 0.7 ºC Fit; R²=0.7977 41.6ºC Fit; R²=0.818 0.6 25ºC Fit; R²=0.9323 0.5-0.4 0.3 0.2 0.1 **Relative Humidity (%)** 0**0** 30 40 60 90 10 20 50 70 80 100 Figure 5.5: Parabolic sorption curves at various temperatures

Unlike ambient pressure, temperature did influence moisture absorption (see Figure 5.5).

The parabolic sorption curve model suggested by Kardos et al. [7] was fit to the data for each temperature using a least-squares regression to determine the value of k_1 at the various temperatures. These three sorption curves are also shown in Figure 5.5. The value of k_1 as a function of temperature is shown in figure 5.6. The linear regression that best fits the data is also shown:

$$k_1 = k_s \cdot (T - T_0)$$
 where $k_s = 1.4 \cdot 10^{-4} K^{-1}$ and $T_0 = -13^{\circ}C$ (25)



Since relative humidity is a function of the vapour pressure of water at a given temperature, we can easily substitute vapour pressure for relative humidity, and this may often be a more convenient approach. This is done in Figure 5.7.



This figure shows that although the equilibrium relative humidity at a given moisture content decreases with increasing temperature, the vapour pressure goes up substantially. The reason that relative humidity decreases with temperature is that the saturated vapour pressure increases with temperature faster than the absorbed moisture's vapour pressure does.

5.5 Moisture Sorption in Open Air

In prepregs some amount of moisture is present in the initial raw material, and additional moisture may be also absorbed from humid air during the thawing, ply cutting, and layup activities [46]. When prepreg is exposed to air - as always occurs during the layup phase of the prepreg process - it will exchange moisture with that air until an equilibrium is reached. This situation is different than what occurs inside a vacuum bag during the debulk phase because there are no pressure gradients driving gas flow inplane. In this situation the mechanism of moisture transport is diffusion. Since fiber-reinforced composite materials are almost always used in sheet format where the in-plane dimensions are much greater than the material's thickness, in-plane diffusion can be neglected and the situation can be approximated as 1 dimensional diffusion occurring in the thickness direction only [63].

Diffusion coefficients can be calculated by measuring the weight of a sample over time in response to a step change in the relative humidity of its environment. This approach assumes 1D diffusion, so the sample must either be in the form of a thin sheet or suitable boundary conditions must be imposed so that the diffusion approximates the 1D case. The initial moisture content of the sample must be uniform. Fickian diffusion is also assumed, although Bond [63] found that the difference in diffusion coefficient predicted using two non-Fickian models was negligibly different from the Fickian case. In response to a step change in relative humidity the weight of the sample changes, quickly at first and then more and more slowly until an equilibrium weight is approached asymptotically.

A useful transformation of the coupon weights is:

$$G = \frac{m - m_i}{m_e - m_i} \tag{26}$$

where m is the sample's weight, m_i is the sample's initial weight, and m_e is the equilibrium weight approached after long times. G can be thought of as a normalized measure of change in moisture content. After the step change in the humidity of a coupon's surroundings the initial value of G is always zero and it increases asymptotically toward 1 as shown in Figure 5.8. When G is plotted in the root-time domain the initial portion of the weight change curve becomes a straight line as shown in Figure 5.9.



Figure 5.9: G in root time domain

The slope of this initial linear region of the curve can be used to determine the diffusion coefficient of the material using the following equation (adapted from [63] and [64].)

$$D = \frac{\pi}{16} \cdot h^2 \cdot m^2 \tag{27}$$

Where D is the diffusion coefficient, h is the thickness of the sample (its dimension in the direction of 1D diffusion) and m is the slope of the initial linear region of G when plotted in the root-time domain. Note that in an inhomogeneous material such as a prepreg this will be an *effective* or *average* diffusion coefficient as the material's internal structure is ignored.

Experiments were performed on both MTM45-1 prepreg and MTM45-1 neat resin. In experiments on prepreg samples of 64mm square and 4 plies thick were used. In experiments on neat resin a small quantity of MTM45-1 epoxy resin was packed into an aluminum sample cup shown in Figure 5.10.



Figure 5.10: Cup used in neat resin moisture absorption experiments

The samples were placed into a closed container that also contained a humidity control medium as described in section 5.1. The humidity control medium was either a saturated sodium chloride solution or a silica gel desiccant. Next, they were placed in a specially constructed enclosure which allows the weight of the parts to be logged over time while enclosed in a container with a humidity control medium (Figure 5.11). Experiments involved both initially dry samples absorbing water, and initially moist samples losing water.



Figure 5.11: Analytical balance with humidity control jig

The logged weights of the prepreg samples were transformed using (26) to obtain the weight change curves in terms of the parameter G. These curves are plotted in the root-time domain in Figure 5.12 and Figure 5.13. A linear model was fit to the initial portion of the data to determine the initial slope. The effective diffusion coefficient was then calculated using (27). Note that the moisture absorption curves for neat resin show greater noise because the neat resin sample's weight was much smaller than the prepreg sample (the total amount of moisture absorbed was ~0.3mg and the scale's accuracy is about 0.05mg) [65].



Figure 5.12: Sorption curve for prepreg in root-time domain



Figure 5.13: Sorption curve for neat resin in root-time domain
The slopes and the corresponding diffusion coefficients determined by this method are shown in Table

5.3.

Sample	Slope m (<i>s</i> ^{-1/2})	Thickness h mm	Calculated Diffusion Coefficient (m ² s ⁻¹)	Notes
Prepreg	0.0053	2.6	$3.7 \cdot 10^{-11}$	Absorption
Prepreg	0.0044	2.6	$2.6 \cdot 10^{-11}$	Desorption
Prepreg	0.0048	2.6	$3.0 \cdot 10^{-11}$	Desorption
Neat Resin	0.0019	1.89	$2.6 \cdot 10^{-12}$	Absorption

Table 5.3: Diffusion Coefficients

This method gives fairly consistent values over the different experiments using prepreg, but the value for neat resin is considerably lower. Relative to the neat resin the prepreg contains both impenetrable pieces (the fibers) and also an interconnected network of gas channels through which moisture diffusion occurs much faster than through resin [66] (Appendix I). The effective diffusion coefficient through prepreg will depend on which of these two competing effects is dominant, and so we must assume a priori that a given prepreg could have either a lower or higher diffusion coefficient than the neat resin it contains.

Assuming Fickian diffusion, the value of G over time is given by [63] [64]:

$$G = \frac{m - m_i}{m_e - m_i} = 1 - \frac{8}{\pi} \cdot \sum_{j=0}^{\infty} (2j + 1)^{-2} \cdot e^{-(2j+1)^2 \cdot \pi^2 \cdot D \cdot t/h^2}$$
(28)

The first 50 terms in the infinite summation were used to plot the curves for G in the figures in this chapter.

A comparison of the predictions of the Fickian model with experimental data is shown in Figure 5.14. As with the absorption of moisture in the samples shown in Figure 5.3, it can be seen that the absorption of

moisture is somewhat variable between different samples. Repeated experiments using the same material do not follow exactly the same curve, and the mass of absorbed water often seems to meander somewhat. Nevertheless, taking an average value measured for the diffusion coefficient the Fickian model is able to predict the moisture uptake to within about ±10% over most of the curve. The results of experiments where absorption occurred (initially dry samples in a humid balance chamber) were not noticeably different than experiments where desorption occurred (initially wet samples in a dry balance chamber).



Figure 5.14: Comparison of sorption data for prepreg samples with Fickian Model

5.6 Moisture Content During Debulk

Moisture is removed from the prepreg during the debulk processing step, but this occurs in a very different way than the exchange of moisture between prepreg and the air during the layup step. During the layup step the broad surface of the prepreg is exposed to the air and there are no in-plane pressure gradients, so it is reasonable to approximate the situation by assuming one-dimensional diffusion in the

thickness direction. During the debulk step the prepreg is not exposed to the air as it is covered by a vacuum bag. Additionally, the vacuum system is extracting gas from the prepreg, and this gas is primarily travelling in-plane through an interconnected network of gas channels present in the prepreg.

A series of 64mm x 300mm by 4 ply laminates were produced, placed in sealed containers with a saturated sodium chloride solution to control the relative humidity level at 75%, and allowed to equilibrate. The laminates were then placed under vacuum bags and debulked for various lengths of time. The vacuum was applied to one edge, with the other edges sealed with butyl rubber sealant tape as shown in Figure 5.15.



Figure 5.15: Arrangement under vacuum bag

Rather than curing the laminates after the debulk, they were cut into smaller pieces, dividing their 300mm dimension into eight pieces. Each piece was immediately weighed, followed by desiccation and reweighing to determine its dry weight. This allowed the moisture content at the end of the debulk step to be calculated using (20). The moisture contents of laminates after various debulk times is shown in Figure 5.16.



The above data represents the average moisture content over the length of the laminate, but the data also includes information about the moisture content profiles in the laminates. The moisture content profiles of laminates after various debulk times are shown in Figure 5.17.



Although the moisture content profiles in these parts are fairly flat, most profiles do show a slightly lower moisture content closer to the breathing edge of the part.

6 Experiments: Variability In Raw Material

Variability in prepreg raw material has been noted as an obstacle to porosity modelling by many authors [9] [51] [47] [48] [49] [50]. An understanding of the nature and range of variation in the raw material is therefore a necessary part of understanding the OOA prepreg process. Here we attempt to characterize variations in the raw MTM45-1/5HS prepreg material used throughout this work.

6.1 Variability Within a Roll of Material

An experiment was conducted to investigate the variability in thickness and moisture content within a single roll of MTM45-1/5HS prepreg raw material. Approximately 130 strips of material were cut from a roll, each strip 64mm wide and spanning the entire width of the roll, about 1.2m, as shown in Figure 6.1.



Figure 6.1: Strips Cut from Material Roll

The location of each strip's original location along the roll (in the warp direction) was recorded. Here a greater "distance along roll" will mean a strip was located closer to the core of the roll. The first strip was arbitrarily assigned a "distance along roll" of zero; however, it should be noted that this location is arbitrary; this roll of material had been used previously for other purposes, and so this zero does not indicate the beginning of the roll.

6.1.1 Initial Thickness Variations

Thickness measurements were taken for each strip of material using a digital micrometer with a precision of $1\mu m$. Because the raw prepreg material contains a film of uncured resin it is soft and sticky, and so taking thickness measurements directly using a micrometer is impractical and produces very inconsistent results. Instead, the thickness measurements were taken by measuring the thickness of the

material as it is supplied on the roll, including the protective layers of paper backing and plastic film. Thickness measurements of the paper backing and plastic film were then taken and these were subtracted from the overall thickness measurements to obtain the initial prepreg thickness.



Figure 6.2: Thickness Variation Along Prepreg Roll

A linear fit to the experimental thickness data (Figure 6.2) shows a decrease in the average ply thickness from 0.525mm to 0.505mm - a decrease of approximately 4% - over 11m of roll length. With the linear overall trend subtracted from the data, the remaining *detrended* data has a standard deviation of $6.5\mu m$. The shaded bands in Figure 6.2 represent one and two standard deviations of the detrended thickness measurements. The detrended data is approximately normally distributed. This is shown in Figure 6.3 where a histogram of the detrended data is compared to a normally distributed frequency function. (This function is the product of the histogram bin width, the number of data points, and a normal PDF with the same standard deviation as the data.)



Figure 6.3: Histogram Plot of Remaining Thickness Variations (σ=6.5 μm)

There is a gap in the data between approximately 8m and 10m "distance along roll" because material was removed from the roll in two batches. Initially about 8m of material was removed from the roll, and a further 1m was cut later, with approximately 2m of material used by other experimentalists in the interim. It is interesting to note that extrapolating the trend in the thickness data for the initial data set predicts the thickness of the material cut later quite well. Additionally, the trend along the entire 11m examined here was decreasing. It is therefore probable that this trend extended beyond the region of the roll examined here, and so the thickness across the entire roll is likely to vary by more than it is observed to here. This is consistent with the previous work of Farhang [9] who measured the thickness of material cut earlier from the same roll of prepreg (equivalent to negative *distance along roll* in our roll coordinate system). Farhang found that the thickness *after* debulking for 7 minutes was 0.53mm. Experiments on this material show that a debulk of 7 minutes decreases the material's thickness by

approximately 5%, so it can be estimated that the initial thickness of this material was approximately 0.56mm.

It was necessary to collect a large number of data points to identify differences in thickness over the length of the roll because there are local thickness variations even between data points located very close together, and also several other sources of uncertainty. The variance in the data can be broken down into its components to see the contribution to the data from variations in thickness over distances of meters, local variability in thickness, and measurement uncertainty.

The linear fit explains about 42% of the variance in the thickness data. The remaining unexplained variance in the detrended data is due to local thickness variations (41% of overall), variations in the thickness of the plastic film and paper backing (12%) and the uncertainty inherent in the measurement itself (5%). The measurement uncertainty is due to the limits of the precision of the micrometer and the difficulty of making consistent measurements because of the softness of the material. The measurement variance was estimated by taking repeated measurements of the same data points.

Data total variance: $7.19 \cdot 10^{-5} mm^2$ $\sigma = 8.48 \mu m$							
Explained variance	Remaining Variance (variance in detrended data): $4.19\cdot 10^{-5}\ mm^2$						
of regression:	$\sigma = 6.47 \mu m$						
$3.00 \cdot 10^{-5} mm^2$	Variance from local	Film + paper backing	Variance from measurement				
$\sigma = 5.48 \mu m$	thickness variations:	thickness variance:	uncertainty:				
	$2.93 \cdot 10^{-5} mm^2$	$0.86 \cdot 10^{-5} mm^2$	$0.4 \cdot 10^{-5} mm^2$				
	$\sigma = 5.42 \mu m$	$\sigma = 2.93 \mu m$	$\sigma = 2\mu m$				

Table 6.1: Components of variance in thickness data

Differences in initial thickness across the width (weft direction) of the roll can also be observed in the experimental data. If the data is separated into the thickness measurements taken on the left hand edge of the roll and on the right hand edge of the roll, thickness variations specific to each edge can be seen superimposed on the overall trend. Figure 6.4 shows the overall linear thickness trend along with cubic

curves fit to the thickness data for each edge. The cubic curves were fit using an iterative nonlinear least squares regression using the software Graph version 4.4.2 [67]. The shaded bands represent \pm 6.5 µm. The line labelled "overall thickness trend" is the linear fit from Figure 6.2.



Figure 6.4: Initial thickness variations along roll edges

A 3rd order polynomial was used to fit the data here because the goodness of fit is much better than for a 2nd order polynomial, but is not substantially improved by using a 4th order polynomial. For example, for the left edge data the coefficient of determination is only $R^2 = 0.063$ for a 2nd order polynomial, but is $R^2 = 0.318$ for a 3rd order polynomial. Using a 4th order polynomial provides only a marginal improvement, with $R^2 = 0.319$.

The average thickness gradient across the width of the roll is steeper than the overall thickness gradient along the roll. Across the width of the roll the thickness changed by about $10\mu m$ over 1.2m, or around $8\mu m$ per meter. Along the roll the thickness changed by about $20\mu m$ over 11m, or about $2\mu m$ per meter.

6.1.2 Initial Moisture Content Variations

Sets of four consecutive strips were stacked together to form into a laminate (for use in other experiments), and a 64mm square portion of each laminate was removed to determine the moisture content. The square portions were weighed, then placed in a container along with a silica-gel desiccant and subsequently re-weighed after allowing adequate time for drying. The weight after desiccation was taken as the *dry weight*, and the moisture content was calculated using (23).



Figure 6.5: Initial Moisture Content Variation Over Prepreg Roll

Substantial variations in initial moisture content were observed. A linear fit to the data shows a decrease in moisture content by a factor of 3.5 across the 11m of the roll examined here. The moisture content varies from 0.14% to 0.04%, an average moisture content gradient of about 0.01%MC per meter along the roll.

As was the case with the initial thickness data above, extrapolating the trend in the initial batch of material predicts the moisture content of the second batch well. Again, the trend is also observed across

the entire region of the roll examined here, and so it can be assumed that material used earlier from the same roll had an even higher moisture content. (Likewise, the material remaining on this roll after the experiments may have had a lower moisture content, although caution must be exercised in extrapolating in this direction as we quickly approach zero moisture content.)

When the linear trend is subtracted the remaining variability in the detrended moisture content data has a standard deviation of approximately 0.02%wt, and appears to be approximately normally distributed, as shown in figure 6.6 which compares a data histogram with a normally distributed frequency function.



Figure 6.6: Histogram Plot of Remaining Moisture Content Variations (σ=0.02%MC)

It is interesting to note that the variation in moisture content is not able to explain the thickness variations discussed in the previous section. Moisture expansion coefficients for epoxy resins are typically on the order of $10^{-3}/\% MC$ [68]. The difference in moisture content observed across the entire

length of the roll, on the order of 0.1%, would produce a thickness change on the order of 10^{-4} , more than two orders of magnitude smaller than the observed thickness variations.

6.2 Variability Between Rolls of Material

The initial moisture content of material from a different roll ("roll #2") of MTM45-1 was measured for comparison with the experiments described above ("roll #1"). The initial moisture content of prepreg in roll #2 was found to average 0.076%, which is within the range observed for roll #1. However, when material from the two rolls was exposed to a controlled humidity level, the amount of moisture absorbed by the two rolls differed. When exposed to a 75% relative humidity environment the prepreg from roll #1 reached an average moisture content of 0.26%, compared to 0.31% for roll #2.

Variability between different rolls of nominally identical material has been a common observation by previous authors. For example, Farhang [9] measured the thickness of material from different rolls of MTM45-1-5HS prepreg after a 7 minute debulk. The thickness was $530\mu m$ for material from one roll, while a different roll was only $460\mu m$, a difference of $70\mu m$ or around 15%. Note that these are much greater variations than the thickness variations observed within one roll above. Farhang also measured the gas permeability of these two rolls to differ by about half an order of magnitude.

This variability in the raw material has long been an obstacle to predicting porosity, as these varying factors can all impact the mechanisms involved in void evolution. It may be necessary for material manufacturers to improve the consistency of the raw materials before a robust predictive capability for porosity will be possible. There may also be variability introduced through the handling, storage, or out-time of these materials, and so it may be necessary to place better controls on these, or for manufacturers to impose standards on incoming material, and to perform acceptance testing related to porosity before material is used to make a part.

67

7 Experiments: Porosity and Process Parameters

Experiments investigating the relationship between process parameters and part porosity are typically conducted by varying the process parameters and observing the influence on part porosity. Given our understanding of the physical mechanisms involved in the processing of OOA prepregs (see Chapter 2.1) we can anticipate which parameters will have an effect on the process. From a process engineering perspective it is useful to categorize these as controllable parameters, non-controllable parameters, and design specifications (Figure 7.1).



Design Specifications

Figure 7.1: Categorization of Parameters

• **Controllable parameters** are the factors under the control of the process engineer, such as debulk time, vacuum level, and humidity. For example, if the humidity of the layup environment is too high a dehumidifier can be installed to reduce humidity. If the vacuum is inadequate the vacuum system can be inspected for leaks, or a new vacuum pump can be purchased.

- Non-controllable parameters are factors that are not under the control of the process engineer, although other parties may have some amount of control over these. For example, the material manufacturer may be able to change the permeability of the material, or its initial moisture content, but the process engineer is not able to affect these (other than by placing conditions on incoming material). The material properties of the initial raw material are non-controllable parameters.
- Design specifications are parameters that are controlled by the part manufacturer, but they are chosen during the design of a part and are not typically able to be modified to suit the manufacturing process. For example, the shape and dimensions of a part are typically fixed by the time the manufacturing process is designed. Note that the process engineer usually does have freedom in choosing where to place the vacuum ports, which will determine the breatheout distance (the effective length scales for gas transport). Some aspects of the cure cycle will be design specifications as well. For example, a part may need to be cured at a certain temperature to ensure the part is able to handle a specified operating temperature, but the ramp rate may have flexibility.

Early experiments on process parameters and their influence on porosity [46] were able to identify qualitative relationships between several process parameters and the porosity of parts produced.



Figure 7.2: Qualitative relationships

In addition to these parameters it is also helpful to include resin pressure as an influencing factor on porosity. Maintaining higher pressure in the resin will tend to produce lower porosity parts by keeping volatiles in solution or forcing them into solution in the resin, and by compressing any gas bubbles present. This is the principal upon which autoclave processing is predicated.



Figure 7.3: Relationship between porosity and resin pressure

In out-of-autoclave processing we have no mechanisms by which to apply additional pressure higher than atmospheric, but there are ways in which resin pressures below atmospheric can be encountered. For this reason the OOA prepreg process is particularly vulnerable to any effect that decreases resin pressure. The atmospheric pressure applied by the vacuum bag is borne jointly by the resin and the fiber bed. Any increase in the pressure borne by the fiber bed constitutes a reduction in resin pressure. Although resin pressure is not measured in this study, it is considered in the discussion of some results as having explanatory power.

7.1 The Problem of Variability

While the author's early experimental data showed that process parameters have an influence on part porosity and suggested the qualitative nature of that influence (ie. does it tend to decrease or increase porosity?) there was clearly enormous variability in the parts as well . The part-to-part variability made these relationships difficult to quantify as two parts made using identical processing conditions will often have very different porosity levels. This suggested one or more of the following:

- The relationships may be highly non-linear
- It may be difficult to control the drivers of porosity
- There is large variation in the non-controllable parameters

In particular, inconsistency in initial raw prepreg is noted often in the previous literature, and variability in the final product of parts have also been attributed to this inconsistency in the initial material [9]. (See Chapter 6 for further discussion of variability in the initial prepreg raw material.) Even for prepregs that are nominally the same product, there can be significant variation between different rolls of material, and even between different parts of the same roll.

There are also several other aspects of experiments on porosity and process parameters that have proven challenging in porosity experiments:

- There are often unwanted variations in the process variables we are trying to control. These can be caused factors such as leaks in the vacuum fittings, the vacuum level achieved by different vacuum pumps, or variations in the moisture content of conditioned parts.
- There may be variations in other more *subtle* process factors that are extremely difficult to control or measure. Since the prepreg process involves a great deal of manual work, some

details of the process may vary with the skill level and experience of the technician. For example, there can be variation in the amount of pressure the technician applies when rolling ply layers together, or in how the technician aligns and stacks the layers of prepreg. Even factors like the sharpness of the knife used to cut the prepreg may have an influence on the process.

7.2 Overcoming Experimental Obstacles

Previous experiments have been confounded by large part-to-part variability and so a large group of experiments was designed with the objective of overcoming the difficulties encountered in previous experiments. This was done by:

- Averaging data over repeats to reduce variability and allow outliers to be identified and removed. Three repeats were conducted under each permutation of process conditions.
- Minimizing variations in the raw material as much as possible by producing all parts from the same roll of material. All plies were cut at the same time, and all parts have similar out-times.
- Producing control parts for each experimental part. The control parts are small laminates cut from the same part of the roll as the associated experimental part and cured under ideal conditions to produce a baseline part matching the experimental part as closely as possible.
 Control parts also allow the moisture content of each part to be accurately measured without having to assume uniformity in the initial moisture content of the prepreg.
- Carefully controlling as many other influences as possible. All experimental parts were produced using the same tool, oven, vacuum pump, and rolls of consumables, and were processed by the same technician (the author).
- Eliminating compaction by manual rolling during layup, as the pressure applied by the technician may not be consistent.

72

- Carefully measuring as many additional parameters as possible so variations in those quantities can be accounted or controlled for eg. the thickness and initial moisture content of all parts.
- Carrying all experiment runs through to completion (including data collection) regardless of any
 problems encountered. This data can give a sense of what kind of problems are encountered
 and how often problems may occur even for an experienced technician producing a simple part.
 It can also allow us to observe how common process problems can affect porosity, and to
 ensure these are consistent with our understanding of the mechanisms involved in prepreg
 processing.

7.3 Experiment Parameters

The parameters varied in these experiments were part length, debulk time and moisture content:

- Parts were all 4 plies thick and 0.064m wide. The lengths were 1m, and 0.3m.
- Parts were debulked for 0.5 hours, 4 hours, or 24 hours.
- Parts were allowed to equilibrate with an environment having a relative humidity of 33% or 75%.

Note: The parameter of vacuum pressure level, which was varied in preliminary experiments, was omitted here. The reason is that in practice, poor vacuum pressure is a problem that is relatively easy for a process engineer to detect and mitigate relative to the other variables. The omission was also necessary for the experiment to have a feasible timeline, as the experimental work presented below took more than one year to carry out.

7.4 Experimental Methods

Experiments were conducted on MTM45-1/5HS prepreg material. As an OOA prepreg it is of the partially impregnated type. The resin film is applied on one side of the reinforcement fibers only, giving the raw material a resin-rich side and a resin-poor side. The fibers used are PAN-based AS4 carbon fibers. This

material was chosen to provide continuity with the large body of research using this material done previously at The University of British Columbia by Louis [26], Hsiao [25], and Farhang [9]. This material is also a good example of a typical OOA prepreg.

7.4.1 Ply Cutting and Layup

Material was initially removed from the storage freezer and allowed a minimum of 4 hours to warm to room temperature. It was then removed from its bag and unrolled. The roll was sliced in the weft direction into pieces 64mm wide strips using a utility knife and a straight edge (Figure 7.4). The strips were numbered sequentially and divided up into the groups that would form the plies for each oven run in the group of experiments. The groups were then placed into individual bags and put back into the freezer.





To produce the laminates for each experimental oven run, the appropriate bag of plies was removed from the freezer and allowed approximately 2 hours to warm to room temperature. The plies were removed from the bag and cut to the length required in the experiment. The protective paper backing and plastic film were then removed from the plies and they were stacked together to form a laminate of 4 plies. The plies were allowed to adhere to each other by their own tackiness alone; they were not rolled or otherwise compacted together.

When each part was laid up a matching control part was also laid up. The control parts were all 64mmx64mm square and 4 plies thick. They were made from material from the same ply numbers as their matching experimental part.

7.4.2 Moisture Conditioning and Humidity Control

After layup all laminates were placed into closed containers having a controlled relative humidity. Humidity control was achieved by the use of saturated salt solutions as described in section 5.1. The laminates were left in the containers for 5 days, which is sufficient time for equilibrium to be achieved between the humidity level of the air in the containers and the moisture content of the prepreg.

Experimental laminates were conditioned in containers with a relative humidity of 33% and 75% using saturated solutions of magnesium chloride and sodium chloride respectively. Measured relative humidity levels were maintained within $\pm 5\%$ of the theoretical relative humidity levels. Control laminates were conditioned in a closed container using a silica gel desiccant.

7.4.2.1 Moisture Content Calculations

The moisture contents of the material just after thawing (subscript i), after desiccation (subscript d) and after humidity conditioning (subscript c) are of interest. An asterisk (*) denotes a control part rather than an experimental part. The initial (immediately after thawing) and final (after 5 days of humidity exposure) weights of the experimental parts was measured. The initial and final (after 5 days of desiccation) weights of the control samples was also measured. All weight measurements were made using a Precisa EP 125SM analytical balance with an accuracy of $\pm 0.05mg$ [65]. From this the initial moisture content can be calculated:

$$MC_i^* = \frac{W_i^* - W_d^*}{W_d^*}$$
(29)

We assume the initial moisture content of each experimental part is the same as the initial moisture content of the matching control part:

$$MC_i^* = MC_i \tag{30}$$

The part's initial weight is known, so its dry weight can be calculated:

$$MC_i = \frac{W_i - W_d}{W_d} \to W_d = \frac{W_i}{MC_i + 1}$$
(31)

Finally the conditioned moisture content can be calculated from the laminate's known conditioned weight and its calculated dry weight:

$$MC_{c} = \frac{W_{c} - W_{d}}{W_{d}} = \frac{W_{c}(MC_{i} + 1) - W_{i}}{W_{i}}$$
(32)

The conditioned moisture content in terms of measured quantities is therefore:

$$MC_c = \frac{W_c}{W_i} \left(\frac{W_i^*}{W_d^*} \right) - 1 \tag{33}$$

7.4.3 Debulk and Cure

After five days of humidity conditioning the laminates were removed from the humidity-control containers. They were immediately placed on a tool and vacuum bagged as quickly as possible to minimize any changes in the material's moisture content during layup. The tool used was an aluminum sheet approximately 3mm thick that was coated with Frekote 700-NC release agent. Laminates were always placed with the resin-rich side against the tool.

The vacuum bag arrangement is as shown in Figure 7.5. The part layup and vacuum bagging was performed according to the following procedure:

- The laminate is placed on the tool.
- A butyl rubber sealant tape is applied around three edges of the part and the perimeter of a pocket where the vacuum port will be located.

- A strip of butyl rubber tape is applied over the laminate about 2cm from the end exposed to the vacuum system (right hand edge in Figure 7.5).
- A non-perforated FEP release-film is placed over the laminate and extends across half the width of the sealant tape. Any air trapped between the laminate and the FEP release film is squeezed out before the seal is complete.
- A cork dam is placed at the end of the laminate exposed to the vacuum system, with dry peelply placed above and below the cork dam and extending approximately 1cm under the end of the laminate.
- Breather cloth is placed in the pocket where the vacuum port will be located.
- The lower (inside-bag) portion of the vacuum port is placed on the breather cloth.
- A nylon vacuum bag is placed over the entire assembly and pressed into all exposed tacky tape.
 Any air trapped between the nylon vacuum bag and the FEP layer is squeezed out before the seal is complete.
- The nylon vacuum bag is slit at the location of the vacuum port and the upper (outside-bag) portion of the vacuum port is installed.

The purpose of this bag arrangement is to simulate the gas transport in a larger part given the limitations of the oven available. By sealing three edges during debulk and cure, gas transport is reduced to an essentially 1D problem, and the breathe-out distance - the distance gas must travel through the laminate to reach an edge exposed to the vacuum system - is increased. (The situation is equivalent to a laminate twice as long, which is exposed to the vacuum system at both ends.) This is achieved by placing sealant tape immediately around the edges of the laminate and pressing it into the laminate's edge. Another strip of sealant tape near the vacuum-exposed edge ensures that the vacuum can only access one end of the part. A cork dam was used at the remaining short edge and strips of dry peel-ply were

used to ensure a gas pathway between the edge and the vacuum port. Breather cloth was also placed between the vacuum port and the cork dam.



Figure 7.5: Vacuum bagging arrangement (nylon bag not shown for clarity)

Note that for each oven run three laminates were placed together on the same tool, and shared a single vacuum port. A typical batch of three 1m long laminates vacuum bagged and ready to be connected to the vacuum pump is shown in Figure 7.6. Note that the shape of the tool allows the parts to sit diagonally in the oven, maximizing the size of parts that can be cured given the size of the oven.



Figure 7.6: Photograph of typical vacuum bag arrangement

The tool was placed into the oven and connected to the vacuum pump. The vacuum seal is then checked by closing a valve to cut the vacuum bag off from the vacuum pump and using a vacuum pressure gauge to ensure there is no observable rise in pressure. Any leaks detected are addressed by pressing the vacuum bag down to ensure it is correctly seated.

After remaining under the vacuum bag for the desired debulk time required by the experiment a programmed cure cycle was started. The cure cycle consisted of a temperature ramp at a rate of 1.5°C/minute to a temperature of 120°C, followed by a 4 hour hold at that temperature. After cooling to a temperature where it could be comfortably handled, the assembly was removed from the oven, the vacuum bag removed, and the cured laminates removed from the tool.

7.4.4 Bulk Porosity Quantification

After curing the bulk porosity was measured for each experimental part. The porosity profiles were measured as a function of distance from the breathing edge. This was achieved by cutting the cured laminates into smaller pieces and measuring the porosity of each piece individually. The 0.3m parts were cut into 6 pieces of 50mm each, and the 1m parts were cut into 10 pieces of 100mm each (Figure 7.7).



Figure 7.7: 1m laminate cut into 10 pieces (*this piece omitted from porosity measurements)

Because of a layer of sealant tape over the first 5cm of the part closest to the vacuum source, the first piece is cut in half again for the 1m parts. The presence of the tacky tape on the piece marked with an asterisk (*) prevents meaningful thickness and density measurements from being taken at this location, and so the first data point represents the 5cm to 10cm interval rather than the 0cm to 10cm interval.

There are several commonly used methods for porosity quantification in composite materials. The merits and limitations of three common methods - the optical microscopy method, the thickness method, and the density method - are compared below. Ultimately the density method was selected as the primary method for quantifying porosity in this experiment.

7.4.4.1 Optical Microscopy Method

This method was used in the preliminary experiments published in [46]. Here laminates were sectioned, polished, and placed under an optical microscope with a motorized stage. Micrographs were acquired and were stitched together to produce a large mosaic image of the microstructure. The porosity was then quantified by analysis of these images.

This method of porosity quantification has the advantage that it can allow the location, size distribution and morphology of the voids to be measured. This method also has several drawbacks:

- It is extremely time consuming. The time required to mount and polish each sample is typically several hours. The time required to align the sample and acquire a mosaic image is also several hours.
- Only the porosity at the location of the sectioning is measured, so it is only valid if the cross section is representative of the entire sample.
- The image analysis produces inconsistent results because the microscope's settings cannot be exactly reproduced each time it is used. Because of this the image analysis settings must be manually chosen each time, producing variable results.
- Since the laminate must be sectioned and mounted it is destructive.

The time consuming nature of porosity quantification by optical microscopy make the technique prohibitive for the present experiments, as it was necessary to quantify the porosity of several hundreds of laminate sections.

7.4.4.2 Thickness Method

It has been shown that thickness measurements can be used to measure the porosity of no-bleed prepreg systems such as the prepreg system used in these experiments [9]. This method uses the fact that the presence of any gas-filled voids will increase the thickness of a laminate. If the thickness of a void-free laminate t_0 is known, the porosity of a porous laminate can be calculated by comparing its thickness *t* with the thickness of the void-free laminate using the following equation:

$$\varphi = 1 - \frac{t_0}{t} \tag{34}$$

The principal advantages of this method are:

- It is very quick and easy to perform, and can be done with inexpensive tools such as a micrometer.
- It is non-destructive.

The main disadvantage of the thickness method is that it tends to have very low accuracy. Obtaining a precise thickness measurement is difficult because:

- The measurements are taken at a single point in the sample, so it is often necessary to take many data points and average them to get a good measurement.
- The anvil faces of most measuring devices (such as calipers or a micrometer) will sit on the asperities of the surface and so actually measure the thickness plus an additional component from the surface roughness. Samples with low roughness are required for precise measurements.
- There are often thickness variations caused by factors other than the porosity, such as variations in the raw material or resin flow during processing. The assumptions of the method require all specimens to have the same theoretical (void-free) density, but this is not usually the case.

The thickness data from 12 laminates made in preliminary experiments are shown in Figure 7.8. This figure shows that for the material used in these experiments (MTM45-1/5HS prepreg) there is significant amount of variability in the composite thickness even after the contribution from voids is subtracted out. Here the porosity was measured using the optical microscopy method and the contribution of the voids to each part's thickness was calculated. (According to the manufacturer's specifications [44], the thickness of a void-free 4-ply laminate is 1550 μ m.)



Figure 7.8: Thickness Contribution of Composite and Voids

The variability in thickness resulting from variability in the composite material itself is greater than the variability in thickness resulting from porosity within the parts. (Porosity levels for these parts range from 0% to 3.9%.)

7.4.4.3 Density Method

The method of using density measurements to quantify bulk porosity was ultimately chosen as the primary method of porosity quantification. The density method is the standard method recommended by ASTM [69] for measuring the porosity of composite materials, and is covered by ASTM standard D2734-94.

The calculation of porosity from density is done in a similar way to the calculation of porosity from thickness. The presence of voids decreases the density of the laminate, and so the porosity can be

calculated by comparing the measured density ρ with the theoretical density ρ_0 . ρ_0 is the density that the composite would have if it was fully dense and contained no voids.

$$\varphi = 1 - \frac{\rho}{\rho_0} \tag{35}$$

Advantages of the density method are:

- It is faster to perform than the optical microscopy method.
- It has been shown to be very accurate.
- It measures the porosity of the entire specimen, rather than just a single slice or point of the specimen.
- It is non-destructive.

The disadvantages of the density method are that it is not as fast to perform as the thickness method, and requires moderately sophisticated equipment such as an analytical balance.

Figure 7.9 shows the porosity profile in a laminate from the preliminary experiments. Comparing measurements taken using optical microscopy and density methods for the sample part, it can be seen that the density method produces much smoother (less noisy) data. The porosity of the 1m part shown was measured every 10 cm.



Note that the optical microscopy (OM) method measures the porosity between pieces (at the cuts), whereas the density method measures the porosity of the entire piece.

All density measurements were made using the method of weighing in air and subsequent re-weighing upon immersion in distilled water, following ASTM D792 [70]. A Precisa EP 125SM analytical balance and the density measurement kit for this balance were used.

7.4.5 Surface Porosity Quantification

The surface porosity of each part was also measured using a photographic method and subsequent image analysis based on the technique used by Wells [35]. The cut pieces of the laminates were photographed in a dark room and illuminated by a uniform light source large enough to subtend the entire area reflected by the laminate's surface from the point of view of the camera (see Figure 7.10). Here an LED panel light backlighting a sheet of paper (acting as a light diffuser) was used for the uniform light source, and other light sources in the room were turned off including the camera's flash.



Figure 7.10: Photographic setup for surface porosity quantification

The photographs were then analyzed using the open-source image analysis software FIJI. The sides of the laminates that were against the tool during the cure cycle were photographed. The light source illuminates the smooth and flat regions of the part well, while the porous regions tend to scatter the light and appear dark in the photographs.

A Nikon D7000 camera was used in this experiment. The parameters and camera settings used are shown in Table 7.1.

Parameter/Setting	Value	
Distance from Camera to Specimen (=Focal Length)	52mm	
F-stop	f/9	
Exposure Time	1/200 seconds	
Flash	No Flash	

Table 7 1.	Parameters and	camera	settings
Table 7.1.	raiameters anu	camera	secungs

Typical images produced with this method are shown below in Figure 7.11. The laminate on the left has low surface porosity (about 0.2%), while the laminate on the right has higher surface porosity (about 7%). The lower images show the porous regions of the laminate identified by the image analysis software.



Figure 7.11: Quantification of surface porosity

Although this method requires some careful trial-and-error to optimize the photographic setup and the image analysis software, this method is very fast once properly set up. This method also produces results that have excellent sensitivity and selectivity to porosity; nearly all voids are correctly identified as voids, and nearly all void-free regions are correctly identified as well. For example, the small stains or discolorations present in on the surface of the laminate on the right in Figure 7.11 have been correctly identified, and not classified as voids.

7.5 Experimental Results

This group of experiments produced a very large and multidimensional data set, and there are many different ways to visualize and slice the data. In total more than 100 laminates were produced for the experiments described below, including more than 60 experimental parts and more than 40 control parts. The weight of each part was measured before and after humidity conditioning, allowing the moisture content of each part to be estimated. More than 400 density and surface porosity measurements were taken on these parts, as well as over 2500 thickness measurements. Successful experiments form the primary data set, but experiments where a problem was encountered were carried through and measurements were taken just as in the successful experiments. This allows insight into the effects that problems encountered during processing can have on a part.

7.5.1 Conditioned Moisture Contents

The moisture content of the laminates after humidity conditioning was calculated by the method described in 7.4.2.1. Laminates exposed to a 33% humidity environment for 5 days had a final moisture content of 0.12% ± 0.012%, while laminates exposed to 75% humidity for 5 days had a final moisture content of 0.256%±0.013%. (Note: Uncertainty values here represent standard deviation in percentage points, not relative standard deviation in percent.) These moisture contents are somewhat different than those measured in the experiments shown in Figure 5.3. Although these experiments both used the same prepreg product, this material was drawn from a different roll of prepreg, and is the result is an example of batch-to-batch variability in raw material.

7.5.2 Bulk Porosity

The simplest way to summarize the experimental bulk porosity data is to look at the average porosity of each group of experimental parts. The average porosity of the three parts made under each permutation of size, debulk time, and moisture content parameters was calculated. The coefficient of variation within each group of three parts was also calculated and whenever this was greater than 20%

88

the part that showed the greatest disagreement with the other two was removed from the average. The resulting porosity data are displayed in figure 7.12 and figure 7.13.



Figure 7.12: Average bulk porosity, 75% Relative Humidity



Figure 7.13: Average bulk porosity, 33% Relative Humidity

The previously established relationships between process parameters and part porosity were

reproduced in this data:

- Parts exposed to higher humidity levels had higher porosity levels.
- Parts that spent longer times under vacuum (longer debulk times) showed lower porosity levels.
- Parts with a greater breath-out distance (ie. longer parts) showed higher porosity levels.
- There is a persistent porosity component of around 0.5% which is difficult to eliminate regardless of processing conditions. Previous authors have associated this component with resin voids: small spherical voids surrounded by resin.
7.5.2.1 Bulk Porosity Profiles

The bulk porosity measurements were taken at various distances along the length of the part, and thus profiles in the porosity along the length of the part were obtained. The distance coordinate here is the distance of the measured point from the breathing edge. The measured bulk porosity profiles are shown in Figure 7.14 to Figure 7.17. Note that the vertical scale of Figure 7.14 is different than the other three plots for readability reasons. Note also that the porosity of the first 5cm of each part is not able to be quantified because of the sealant tape on the part at that location, part of the vacuum bagging arrangement (see Figure 7.7).



Figure 7.14: Bulk porosity profiles in 1m parts exposed to 75% relative humidity



Figure 7.15: Bulk porosity profiles in 1m parts exposed to 33% relative humidity



Figure 7.16: Bulk porosity profiles in 0.3m parts exposed to 75% relative humidity



For the majority of parts, the bulk porosity increases with greater distance from the vacuum system. The bulk porosity profiles in the 1m parts increase for some distance before reaching a plateau. This is consistent with the findings of Farhang [9], who observed differences in porosity levels between the region near the vacuum system and the region deep within the part, and noted that these porosity gradients began to appear at approximately the same time the resin reaches its minimum viscosity.

In the 1m parts the bulk porosity is also seen to decrease somewhat at the point farthest from the breathing edge. This is apparent not only in the averaged data (see Figure 7.14, Figure 7.15) but is actually present in the data for every individual 1m part. Figure 7.18, for example, shows the 3 individual parts comprising the 1m length, 75% relative humidity, 0.5hr debulk time data set.



Figure 7.18: Example of bulk porosity decrease at most distant data point in 1m parts

This is a feature that has been present in data from previous experiments as well, where it was dismissed as an artifact [46]; however, its ubiquity in the current data set strongly suggests this a real feature of the data and not an artifact. The cause of this feature is not known and no plausible mechanism that would produce this effect has yet been suggested.

In the 0.3m parts the bulk porosity profiles are less pronounced. The parts that were exposed to 75% relative humidity are still clearly affected by varying the debulk time, but the parts exposed to 33% relative humidity are not well distinguished from each other, and here the porosity levels for each debulk time are mostly within the error bars of the other parts. A decrease in porosity at the last data point is not observed in the 0.3m parts as it is in the 1m parts.

7.5.3 Surface Porosity

The levels of surface porosity were measured using the technique described in 7.4.5. The surface porosity levels averaged over the length of the parts and over repeated runs are shown in Figure 7.19 and Figure 7.20.



Figure 7.19: Average surface porosity, 75% Relative Humidity



Figure 7.20: Average surface porosity, 33% Relative Humidity

The surface porosity data resembles an "exaggerated" version of the bulk porosity data: laminates with bulk porosity lower than about 1% have very low or negligible surface porosity, while laminates with higher bulk porosity have surface porosity levels greater than the bulk porosity.

Plotting the bulk porosity data against the surface porosity data we see this effect more clearly (Figure 7.21). Surface porosity does not begin to appear until the bulk porosity reaches about 0.5%-1%. Above this level surface porosity increases about twice as quickly as bulk porosity does. A linear regression fits the relationship between surface porosity and bulk porosity well.



Figure 7.21: Relationship between bulk and surface porosity

Because surface porosity is essentially zero at low bulk porosity levels the regression has a nonzero intercept along the bulk porosity axis. The intercept with this axis is the level of bulk porosity above which surface porosity is seen. A linear regression on the data for both the 0.3m and 1m laminates is shown in Figure 7.21, and the intercept corresponds to a bulk porosity of 0.59%. This number is very robust over the two data sets; the same regression using data from parts grouped by length yields very similar results:

Data Set	Intercept
1m and 0.3m	0.59%
1m only	0.51%
0.3m only	0.55%

Table 7.2: Intercept calculated from different data sets

This result may be especially useful because aerospace parts typically have an upper limit on the bulk porosity level specified, usually around 1%-2%. In the experimental data the parts with no surface porosity had bulk porosities averaging 0.59%, and always had a bulk porosity of less than about 1%. If the results of this study are typical, and the absence of surface porosity would always indicate a bulk porosity level of about 1% or less, that would make surface porosity an extremely useful proxy for bulk porosity.

7.5.3.1 Surface Porosity Profiles

The surface porosity profiles in the experimental parts qualitatively resemble the bulk porosity profiles. Like bulk porosity, surface porosity tends to be lowest near the breathing edge, and increases with increasing distance from the breathing edge before reaching a plateau. Surface porosity profiles are shown in Figure 7.22 to Figure 7.24. Note that all three plots have different vertical scales. The 0.3m parts have been combined on a single plot because the surface porosity levels of the 0.3m parts exposed to 33% relative humidity are negligible.







Figure 7.23: Surface porosity profiles in 1m parts exposed to 33% relative humidity



Figure 7.24: Surface porosity profiles in 0.3m parts exposed to 75% and 33% relative humidity

When the bulk and surface porosity profiles are plotted together it is apparent that in addition to the overall shape, smaller peaks and valleys in porosity level are common to both the bulk and surface porosity profile data (see Figure 7.25, to Figure 7.30). Note that unlike all the above plots of porosity levels, which have been averaged over three parts, the porosity profiles below correspond to individual parts.





Figure 7.25: Comparison of bulk and surface porosity profiles (1m, 75% relative humidity, 0.5hr debulk, part A)

Figure 7.26: Comparison of bulk and surface porosity profiles (1m, 75% relative humidity, 0.5hr debulk, part B)



Figure 7.27: Comparison of bulk and surface porosity profiles (1m, 75% relative humidity, 0.5hr debulk, part C)



Figure 7.28: Comparison of bulk and surface porosity profiles (1m, 75% relative humidity, 4hr debulk, part A)



Figure 7.29: Comparison of bulk and surface porosity profiles (1m, 75% relative humidity, 4hr debulk, part B)



Figure 7.30: Comparison of bulk and surface porosity profiles (1m, 75% relative humidity, 4hr debulk, part C)

In these plots the it can be clearly seen that the surface porosity profile consistently intersects the bulk porosity profile at around 1%. Surface porosity profiles resemble bulk porosity levels that have been increased when greater than 1%, and decreased when less than 1%.

The presence and coincidence of minor "peaks and valleys" type features across both data sets suggest several interesting things:

- It suggests that these features are not due to measurement uncertainty but are real variations in porosity levels within the parts.
- It demonstrates the extent to which surface porosity and bulk porosity are related.
- It indicates that the measurement technique used is sensitive enough to resolve these smaller features in the porosity data.

The feature seen in the bulk porosity data for 1m parts where the porosity decreases at the single data point furthest from the vacuum system is not mirrored in the surface porosity data. Since other features are common to both data sets, this suggests the unknown cause of this feature acts to reduce bulk porosity at this location without affecting surface porosity.

7.5.4 Effect of Resin Bleed and Resin Pressure Loss

The MTM45-1 5HS prepreg system used in the present experiments is a net-resin prepreg, meaning that the quantity of resin present in the raw material is the quantity intended to be present in the final part; no resin is intended to be removed or "bled" during processing. It is for this reason that a cork dam is placed under the vacuum bag at the breathing edge of the part - to prevent resin from being drawn out by the vacuum system. This is important because a loss of resin will cause the pressure from the vacuum bag to be transferred to the fiber-bed with a corresponding loss of pressure in the resin. A loss of resin pressure has been shown to lead to void stabilization and growth [35].

To investigate the effect of resin bleed and the resulting loss of resin pressure a series of experiments were conducted on very small laminates. Even with a dam in place a small amount of resin is inevitably absorbed by the dam and by other vacuum bagging consumables such as the peel-ply. The amount of resin lost is never exactly zero, but it is usually a negligible fraction of the total resin in the part. If a very

small part is made, however, the tiny amount of resin lost can be a significant fraction of the total resin in the part.

Parts were produced in an identical manner to the 1m and 0.3m parts described above except with a length of only 0.1m. The dam is identical for parts of all size, but for these small parts the quantity of resin bled was a non-negligible fraction of the part's total resin content, and the impact of this on the part densities and porosity levels was measurable.

7.5.4.1 Quantifying Resin Bleed

During the curing of a set of 0.1m laminates the quantity of resin bled into the peel ply and cork dam was measured.



Figure 7.31: Measurement of resin bled into peel ply

The quantity of resin bled into the peel ply was estimated by measuring the thickness and width of the peel ply strips and the depth into which resin has impregnated the peel ply (see Figure 7.31). Averaged over three laminates this "resin impregnated" volume was approximately $140mm^3 \pm 14mm^3$. If we assume the resin volume fraction of the resin impregnated peel ply is about 50%, this corresponds to about $70mm^3 \pm 7mm^3$ of resin, or about $80mg \pm 8mg$ of resin.

To estimate the quantity of resin bled into the dam, 45mm wide segments of cork dam were isolated by wrapping them in peel-ply. These sections of dam were then weighed before and after use in the cure of a 0.1m laminate (see Figure 7.32). The initial and final weights of the two repeats are shown in Table 7.3.

Table 7.3: Resin bled into cork dam

	Initial Weight (g)	Final Weight (g)	Resin Absorbed (mg)
Cork Dam 1	1.22391	1.33425	110
Cork Dam 2	1.25565	1.34785	92

Each 45mm segment of cork dam absorbed about 100mg of resin.



Figure 7.32: Measurement of resin bled into cork dam

The full width of the cork dam is 64mm, so scaling the quantity of absorbed resin up accordingly, the entire width of the cork dam is estimated to absorb about 140mg of resin.

In these experiments the cork dam appears to have absorbed about two thirds of the bled resin, with the peel ply absorbing the remaining one third.

Table 7.4: Comparison of resin bleed estimates

	Resin Bleed
Absorbed by Dam	140 <i>mg</i>
Absorbed by Peel-ply	80 <i>mg</i>
Total Measured	220mg

7.5.4.2 Effect on Laminate Density

For a laminate where both the density and thickness are known the areal density can be calculated, and this can be useful in identifying if any of the laminates has experienced any resin bleed. The presence of voids in a laminate has the effect of both reducing the density and increasing the thickness of a laminate. The product of these quantities; however, is identically its areal density and is not affected by the presence of voids.

The areal density of a prepreg is the sum of the mass of fibers per unit area and the mass of resin per unit area. (We will assume that the gas within any voids has negligible density.) It is also assumed that the fibers do not move during processing, and so any change in areal density is due to a change in the quantity of resin per unit of area. Any resin bleed can therefore be identified by a decrease in areal density as calculated by multiplying the thickness and volumetric density data together.

Using this method to compare the data sets from the 1m, 0.3m and 0.1m parts we can see that the areal density of the 1m and 0.3m parts do not differ significantly, but the areal density of the 0.1m parts is lower than the other two (see Figure 7.33).

105



Figure 7.33: Areal density of experimental parts grouped by length

The areal density of the 0.1m parts is lower than the other parts by about $35g/m^2$, or 223mg of "missing" resin in a part this size. This agrees very well with the estimate of bled resin from the previous section of 220 mg.

The areal density of just the resin in a 4-ply MTM45-1 laminate is $840g/m^2$ [44], so we can estimate that about 4% of the resin was bled from the 0.1m parts.

7.5.4.3 Effect on Porosity Levels

The porosity levels in the 0.1m parts were quantified using the same procedure as the larger parts, except that the parts were not divided along their lengths, and only a single value was measured rather than a profile along the length of the parts. The 0.1m parts show the same relationship to debulk time as the larger parts do, with both bulk and surface porosity decreasing with longer debulk times. The porosity levels are shown in Figure 7.34 to Figure 7.37.



Figure 7.34: Bulk porosity, 75% relative humidity



Figure 7.35: Bulk porosity, 33% Relative Humidity



Figure 7.36: Surface porosity, 75% Relative Humidity



Figure 7.37: Surface porosity, 33% Relative Humidity

This data does show a departure from the usual relationship with part size where longer parts tend to have greater porosity. Many of the porosity levels in the 0.1m parts are substantially higher than they are in the larger 0.3m and 1m parts. It is hypothesized that this is the result of void growth caused by reduced resin pressure relative to the longer parts.

The parts that were both exposed to the lower (33%) relative humidity level and debulked for 4hr, as well as all parts that were debulked for 24 hr, exhibited quite low porosity levels despite the reduced resin pressure. There is reason to think that these parts were almost completely dried during the debulk processing step, and this very dry condition with negligible resin moisture content may explain why this was the case. (See section 9.7 for further commentary on this.)

7.5.5 Case Studies of Problems Encountered in Debulk and Cure

The experiments described above represent parts that encountered no apparent problems during the layup, debulking, cure and measurement of the parts; however, not every attempt to cure a batch of parts was successful during this project. Instead of discarding a part when a problem was encountered during processing all parts were processed to completion and all measurements were taken as if no problem had been encountered. Doing this allows us to characterize not only what occurs during the OOA prepreg process when everything goes according to plan, but also what difficulties can be encountered during processing and how these affect the final parts. This is important information because the OOA prepreg process can often experience high reject rates relative to other composite manufacturing processes, especially due to the precise and intricate nature of the necessary vacuum bagging procedures [71]. For academic researchers these can be regarded as interesting case studies. For practitioners - process engineers and technicians - they can be seen as experience that might aid in diagnosing a problem in a process, or deciding if a batch of parts that experienced a processing problem must be rejected or not. The problems that were encountered in the course of conducting the porosity experiments are described below, along with the effect the problem had on the parts produced.

109

7.5.5.1 Leak at Vacuum Fittings

A batch of 1m long parts had been exposed to 75% relative humidity. During the 24 hour debulk and cure there was a leak in the vacuum system. The leak was not detected during the cure cycle, but the cured parts showed unexpectedly high surface porosity levels. The vacuum system was inspected by using valves to isolate sections of the vacuum system and using a vacuum gauge to test each section for leaks. During this inspection it was discovered that a vacuum hose had a faulty fitting that leaked intermittently depending on the position of the hose. The actual vacuum level seen by the parts during debulk and cure is not known.

Both the surface and bulk porosity levels of these parts are much higher than would be expected if there had been no leak in the vacuum system (see Figure 7.38, Figure 7.39). Additionally, the surface porosity levels were not higher than the bulk levels, as was the case in the experimental parts that were cured without problems.



Figure 7.38: Effect of leak at vacuum fittings on bulk porosity profiles (1m, 75% relative humidity, 24hr debulk)



7.5.5.2 Cure Interrupted, Vacuum Released

A batch of 1m long parts had been exposed to 75% relative humidity and debulked for 24 hours. During the cure cycle a problem with a thermocouple caused an error condition in the oven's temperature controller and the temperature controller aborted the cure cycle. It was not known at what point during the cure cycle this occurred, so the part and vacuum bag were separated from the tool at two opposite corners (shown by arrows in Figure 7.40 and Figure 7.41) to inspect the parts. One corner of part A was lifted at the end farthest from the vacuum port (A) while one corner of part C was lifted at the breathing edge. Part B was not lifted from the tool and the tacky tape surrounding it remained adhered to the tool.



Figure 7.40: Arrows indicate locations where layup was lifted from the tool part way through the cure cycle

The surface of the parts appeared solid and could not be indented by a fingernail. The surface was smooth and it appeared that resin had at least partially infiltrated the reinforcement; however, the corners of the parts responded viscoelastically when released, returning to their flat configuration slowly. This indicated that the cure cycle did not run to completion before the error occurred and so the part and vacuum bag were reseated on the tool and the cure cycle was restarted. The temperature ramp to 120°C was completed, but the error recurred shortly afterward. The thermocouple was repositioned slightly and the cure cycle was restarted again, this time running to completion.

The regions where the corners had been lifted showed a visibly rough surface finish (highlighted in Figure 7.41). Part B had a smooth surface finish and no surface porosity, as did the regions of parts A and C outside the highlighted regions.



Figure 7.41: Tool-side surfaces of parts with regions showing a rough surface finish highlighted

The region of part A exhibiting surface roughness begins about 50cm from the breathing edge and extends to the end of the part. On part C the region with surface roughness begins at the breathing edge and extends approximately 40cm into the part. The morphologies of these two regions are very different, and are compared in Figure 7.42.



Figure 7.42: Comparison of morphology of surface porosity on tool side of parts A and C

The region of part A that had been lifted from the tool at the end farthest from the vacuum port has a rough texture everywhere. The surface that had been lifted at the breathing edge was smooth everywhere except at the fiber tows that run in the long direction of the part (this is the weft direction on the original roll or material). The rough surfaces in these regions are not due to surface porosity, but they do prevent surface porosity from being measured using the technique described in 7.4.5, as the non-porous region does not provide the specular reflection required for the technique to work.

The bulk porosity profiles of these parts are shown in Figure 7.43. The bulk porosity of part A near the breathing edge is similar to a normally cured part but in the region where the laminate was lifted from the tool the bulk porosity is about 4 times higher. A sudden jump in porosity corresponding to this region can be seen clearly in the part's bulk porosity profile. In part B the edges remained sealed and the laminate remained seated against the tool during, and the porosity levels measured in this part are not substantially different than the porosity levels in a normal part. The porosity profile of part C does not exhibit the sudden jump seen in part A; however, the porosity level is somewhat elevated relative to a normally cured laminate.



Figure 7.43: Comparison of bulk porosity profiles of normal parts with parts A, B, C (1m, 75% relative humidity, 24hr debulk)

7.5.5.3 Compromised Vacuum Seal

A batch of 1m long parts had been exposed to 75% relative humidity, debulked for 24 hours and cured. Upon removal from the tool it could be seen that some stray fibers had bridged the sealant tape along one long edge of the layup. The vacuum there was clearly compromised, and the laminate adjacent exhibited visible surface porosity. The seal was compromised at two locations approximately 32cm and 39 cm from the breathing edge as shown in Figure 7.44.



Figure 7.44: Stray fibers bridging the vacuum seal

The bulk and surface porosity profiles of this part are shown in Figure 7.45 and Figure 7.46. Both are elevated compared to a part cured without a compromised vacuum seal.



Figure 7.46: Effect of compromised vacuum seal on surface porosity profile (1m, 75% relative humidity, 24hr debulk)

Bulk porosity levels are highest in the region surrounding the leaks and decreases toward both ends of the part. Surface porosity is highest between the region of the leaks and the breathing edge and decreases substantially toward the far end of the part. The other two parts cured in the same layup did not appear to be affected, and exhibited no surface porosity and very low bulk porosity.

7.5.5.4 Minor Vacuum Leak

A batch of 0.3m and 0.1m parts were exposed to 33% relative humidity. When the vacuum bag was connected to the vacuum pump it was apparent that that there was a vacuum leak. It was unusually difficult and time consuming to locate and eliminate the leak, and it was suspected that there were some ongoing minor leaks remaining in the system. The source could not be determined; this is a common symptom of pinhole leaks in the bagging consumables. After curing, the parts were removed from the tool and vacuum bag and a high level of visible surface porosity immediately confirmed that there had been a problem achieving hard vacuum during the debulk and cure.

The bulk and surface porosity profiles of the 0.3m parts are shown in Figure 7.47 and Figure 7.48. The porosity levels of the 0.1m parts are shown in Figure 7.49. All porosity levels are elevated compared to a normal cure cycle, but not as dramatically as in the cases of leaking fittings and compromised vacuum seals discussed above, which probably involve leaks of substantially greater magnitudes.



Figure 7.47: Effect of minor vacuum leak on bulk porosity profile (0.3m, 33% relative humidity, 4hr debulk)



Figure 7.48: Effect of minor vacuum leak on surface porosity profile (0.3m, 33% relative humidity, 4hr debulk)



Figure 7.49: Effect of minor vacuum leak on porosity levels of 0.1m parts (33% relative humidity, 4 hr debulk)

8 Scaling Relationships

For parts where the breathe-out distance is large the evolution of voids is governed primarily by the gas transport processes removing gas and vapours from the prepreg. This is because for these parts the gas flow transport mechanisms operate on much longer time scales than diffusion (See section 4.3, especially Figure 4.5). For the MTM45-1/5HS prepreg studied here this is true for parts where the breathe-out distance is larger than about 0.25m. For parts where this is the case we expect there to be a relationship between the breathe-out distance of the part and the debulk time required to achieve a specified level of porosity in that part. In Darcy's law, as with many transport phenomena, the time scales involved are proportional to the square of the length scales (See equations (9), (11)). This suggests that the following quantity may be a useful indicator of performance in an OOA process:

$$\zeta = \frac{L^2}{t_{debulk}} \tag{36}$$

where L^2 is the breathe-out distance and t_{debulk} is the debulk time. It is suggested that all else being equal, laminates that have similar values of ζ should have similar porosity levels and that in general porosity level should be a monotonic function of ζ .

In Figure 8.1 the measured bulk porosity data for the laminates equilibrated with a 75% relative humidity environment are shown as a function of ζ on a semi-log plot. Within the variation in the porosity data the data does indeed increase monotonically with ζ , and in fact the relationship is almost linear. A linear fit to the data is included on the graph (note that the linear fit is distorted by the semi-log plot.)

The bulk porosity data for the laminates exposed to a 33% humidity level are shown in Figure 8.2. The data are consistent with this approach but are not as compelling as the porosity levels here are all very

low and the variations in porosity are mostly due to part-to-part variations rather than the varying of process conditions.

The same approach can be taken for surface porosity and the results are shown in Figure 8.3 and Figure 8.4.



Figure 8.1: Linear fit to measured bulk porosity vs ζ for laminates exposed to 75% relative humidity



Figure 8.3: Linear fit to surface porosity vs ζ for laminates exposed to 75% relative humidity



Figure 8.4: Linear fit to surface porosity vs ζ for laminates exposed to 33% relative humidity

The points of greatest interest are the data from one size of part with values of ζ that fall between parts of another size, because it is already known that for parts of a given size, longer debulk times tend to produce parts with lower porosity levels. In particular these are the points representing 0.3m parts with a 0.5 hour debulk time and 1m parts with a 24hour debulk time. From these points we can see that the ζ parameter appears to place the parts of different size in the correct order.

This approach provides a simple method of comparison for parts of different sizes and could be useful in the scaling up of small scale materials tests to larger full-scale parts.

9 Numerical Model

In 1986 Kardos [7] emphasized the complexity of the void phenomenon and articulated the difficulty in approaching the problem by attempting to directly solve the equations representing the relevant transport phenomena. Here a model is presented that takes us one step closer to the ability to model this complex process.

A numerical model was derived by coupling together the equations that describe the physical phenomena occurring during the debulk step of OOA prepreg processing that are most important in governing the evolution of porosity. (These are described in Chapter 4). This model is intended to complement the experimental work discussed in chapter 7, and to investigate the practicality of estimating part porosity levels by simulating these transport phenomena. This model should be considered a preliminary step toward porosity modeling, used to determine if a model produced from coupling previously suggested sub-models together can produce results consistent with the results measured in experiments.

At the outset of development of the model the prediction of post-debulk resin moisture content was considered a good benchmark for performance of this model. If such a model could also estimate porosity values of the correct order of magnitude with a minimum of - or entirely without - fitting parameters to the experimental data itself, that was considered to be a sign that this type of modelling showed promise. Both of these goals have been achieved by this model.

The model is not a representation of all the physical phenomena known to be important in OOA processing. Indeed, it is not currently feasible to do this because not all of the relevant physical phenomena involved are well understood yet. For example, although the work of authors such as Kardos et al. [7] and Wells [35] has shed light on the conditions under which high resin moisture contents are expected to lead to void growth during the cure step of processing, we are not yet able to consistently predict when this will occur in experiments, and we do not yet understand what the rate of

123

void growth or the final size of voids will be. For this reason the model is currently restricted to

modelling the debulk processing step and is not currently able to simulate the cure step.

It is hoped that this model's predictive capability can eventually be extended through the cure cycle. In particular, this will require building a more complete understanding of the relationship between void growth, dissolved moisture, and resin pressure at temperatures encountered during the cure. Our current understanding of this area is summarized in Table 9.1.

Table 9.1: Current understanding of void evolution during of	ure
--	-----

Question	Current Understanding
What conditions (temperature, resin pressure, and resin	Well Understood
moisture content) will lead to moisture-driven void growth	(Kardos criterion)
during cure in neat resin?	[7] [35]
What conditions (temperature, resin pressure, and resin moisture content) will lead to moisture-driven void growth during cure in prepreg laminates?	Predictions agree with experiment below 120ºC but not at 180ºC. [35]
How much will the porosity increase due to moisture-driven void growth during the cure? (Rate of growth, final void size etc.)	Not understood
How does resin bleed/reduced resin pressure affect moisture- driven void growth during the cure?	Not understood

The element under consideration in the model is shown in Figure 9.1. The physical mechanisms and submodels used to describe them in the model are as follows:

• The flow of gasses through the interconnected network of gas channels is described by Darcy's

law. The Klinkenberg correction for Darcy's law was found to be important here and is included

as well.

- The equilibrium between the partial pressure of the water vapour component of the gas and the moisture content of the resin at the surface of the gas channels is described by Kardos' parabolic sorption curve [7].
- The transport of moisture from deep within the resin to the surface of the resin is described by Fick's law. In this model it is represented as a single Fick's law element to simplify the model.

- Like the gas flow, the flow of the resin film into the porous region of the fiber bed is described by Darcy's law; however, since the resin is a liquid the Klinkenberg correction is not used.
- The degree of infiltration of the resin and the gas permeability of the material are assumed to be related. The initial value of the permeability is given by the measured permeability value for the material, and it decreases proportionally as resin infiltration proceeds, going to zero as resin infiltration is complete (when the porosity is reduced to zero).
- Gas transport is assumed to be 1D. Note that in the experiments described in the preceding chapters boundary conditions were imposed that restricted the gas flow in the experiments to a 1D case as well.



Figure 9.1: Element considered in the model

The dependent variables in the model are shown in Table 9.2. These are solved over time and over the 1D spatial coordinate in the part. As with the experiments in the preceding chapters the breathing edge is taken as zero, with increasing values representing regions of the laminate farther from the breathing edge.

Table 9.2: Dependent variables in model

Variable	Variable in MATLAB	Meaning
P_a	u(1)	Partial pressure of air
$P_{_W}$	u(2)	Partial pressure of water vapor
β	u(3)	Resin infiltration parameter
MC_R	u(4)	Resin moisture content

The mathematical model was implemented in MATLAB³ using that software's built in PDEPE partial differential equation solver. This is a finite-difference based solver capable of solving systems of PDEs over time and one spatial variable. PDEPE will select the time step dynamically, but does not automatically refine the spatial mesh. The source code used is included in Appendix H.

The resin infiltration parameter β is a parameter that can be thought of as describing the degree of infiltration of the resin into the fiber region. If a resin film were sitting on top of the fiber bed this parameter would be equal to 0 (see Figure 9.2). This parameter increases as resin infiltration of the fiber bed proceeds, and goes to one as porosity goes to zero (when resin infiltration is complete.)



Figure 9.2: Physical meaning of parameter beta

³ MATLAB Version 7.10.0.499 (R2010a) was used.
It is useful to define a complementary parameter γ where:

$$\gamma = 1 - \beta \tag{37}$$

This parameter can be interpreted as a "relative porosity". We define it to be the current porosity of the fiber bed region relative to the porosity of the fiber bed if no resin were present. β is then defined by (37). Note that the initial value of β is not necessarily 1. In the MATLAB code γ is a dependent variable, but β is used in the discussion because it has a more intuitive meaning.

To model the closing up of gas channels as resin infiltration proceeds, we assume the gas permeability is directly proportional to the porosity:

$$K_{eff} = K_g \cdot \frac{1 - \beta}{1 - \beta_0} = K_g \cdot \frac{\gamma}{\gamma_0}$$
(38)

The input parameters required by the model are shown in Table 9.3, along with the values used for simulations of MTM45-1 material and the sources of these values. The details of how some of these values are calculated can be found in Appendix E.

Table 9.3: Input parameters required in model

Variable in	Variable in	Value	Meaning	Notes/Source		
Derivation	MATLAB					
K _g	Кg	$1 \cdot 10^{-13}$	Gas permeability (longitudinal) in m ²	(MTM45-1 5HS Prepreg - Estimated from theory and experiments. Note that the roll used in these experiments has a relatively high permeability compared to other rolls of the same material.)		
K ₁	кі	$1 \cdot 10^{-15}$	Liquid permeability (radial tow) in m ²	(MTM45-1 5HS Prepreg - Estimated from theory and experiments)		
μ_{a}	mua	$1.86 \cdot 10^{-5}$	Air viscosity in Pa s	(From Gas Viscosity Calculator http://www.Imnoeng.com/Flow/GasViscosity.p hp)		
μ_w	muw	$9.9 \cdot 10^{-6}$	Water vapor viscosity in Pa·s	(From NIST chemistry webbook http://webbook.nist.gov/chemistry/)		
μ_l	mul	23400	Resin viscosity in Pa·s.	(From Raven, MTM45-1 @25ºC)		
ϕ_{g}	phig	0.35	Initial void space volume fraction (porosity).	(Estimated from experiments with MTM45-1 5HS Prepreg)		
$\phi_{\it fiber \ bed}$	phibed	0.46	Porosity of fiber bed region (Porosity of dry fabric only if no resin were present.)	(Estimated from Umeco MTM45-1 Data Sheet)		
h_f	hbedt	$1.8 \cdot 10^{-4}$	Half thickness of fiber bed in m.	(Estimated from micrographs of MTM45-1 5HS.)		
P _{atm}	p0	101300	Initial pressure in Pa	(1 atmosphere in Pa)		
γ ₀	gamma0	0.9	Initial relative porosity (=1-initial degree of resin infiltration)	(Estimated from MTM45-1 Prepreg Spec Sheet Data)		
$\gamma_{ m lim}$	gammalim	$5 \cdot 10^{-3}$	Lower limit on gamma to avoid numerical instability.	(Must be close to zero.)		
P_{∞}	pinf	101300	Atmospheric pressure on vacuum bag.	(1 atmosphere in Pa)		
<i>k</i> ₁	k1h2o	0.00558	Parameter for parabolic sorption curve.	(Originally from Kardos, 1986, agrees with experiments on MTM45-1 5HS prepreg)		
R	R	8.314	Molar gas constant in m ³ ·Pa/mol/K.	(Physical constant)		
M _{H20}	mh2o	0.018	Molar mass of water in kg/mol.	(Molar mass of H2O)		
M _{air}	mair	0.02897	Molar mass of dry air in kg/mol.	(Molar mass of dry air)		
$ ho_{0dry}$	rho0dry	1098	Density of dry pre- preg when gamma=1 in kg/m ³	(Calculated from thickness, density data)		
k _D	kD	0.12	Parameter for diffusion rate, units of kg/m ³ /s.	(Calculated from diffusion coefficient, prepreg microstructure. See Appendix E)		
b	b	13000	Klinkenberg parameter in Pa.	Estimated from (7) [72]		

The processing parameters of interest - the parameters varied in the experiments above - are shown in Table 9.4. Note that length does not appear in the derivation because it only appears in the model when creating the 1D mesh for the differential equation solver.

Variable in Derivation	Variable in MATLAB	Meaning	
Does not			
appear	I	Length of laminate	
T		Temperature of debulk to be	
	t0	simulated.	
MC_0	mc0	Initial prepreg moisture content	

Table 9.4: Procesing parameters

9.1 Model Derivation

The model assumes that the fibers do not move during processing. Resin is assumed to infiltrate the fiber bed in the thickness direction, but is assumed not to move in-plane. Only gasses are assumed to be transported in plane during processing. The continuity equation for a component i of the gas within the laminate is

$$\frac{\partial}{\partial t} \left(\rho_i \cdot \phi_g \right) + \nabla \cdot \left(\rho_i \cdot \phi_g \cdot \vec{v}_g \right) = \dot{m}_i$$
(39)

where ρ_i is the density of component i of the gas, \vec{v}_g is the gas velocity, and \dot{m}_i is a source term - the mass of gas component i generated per unit of time per unit of volume.

Combining this with Darcy's law (1) and the ideal gas law gives us the equation describing gas transport within the laminate:

$$\frac{\partial}{\partial t} \left(\frac{P_i \cdot M_i}{RT} \cdot \frac{\gamma}{\gamma_0} \cdot \phi_{0g} \right) - \nabla \cdot \left(\frac{P_i \cdot M_i}{RT} \cdot \frac{K_g}{\mu_g} \sum \vec{\nabla} P_i \right) = \dot{m}_i$$
(40)

To obtain an expression for \dot{m}_i we approximate Fick's law by ignoring transients and consider a single Fick element carrying diffusing moisture from deep within the resin to the interface between the resin and the vacuum channels. The result is that the rate of mass transport from deep within the resin to the interface between the resin and the vacuum channels is directly proportional to the difference in moisture content between the bulk resin and the resin adjacent to the vacuum channels:

$$\dot{m} \propto \left(MC_r - MC_v\right) \rightarrow \dot{m} = k_D \cdot \left(MC_r - MC_v\right)$$
(41)

Combining (40) with (38), and (41), and applying the Klinkenberg correction (6) to K_g as well gives the equation describing how each gas component pressures changes with time:

$$\frac{\partial}{\partial t} \left(\frac{P_i \cdot M_i}{RT} \cdot \frac{\gamma}{\gamma_0} \cdot \phi_{0g} \right) - \nabla \cdot \left(\frac{P_i \cdot M_i}{RT} \cdot \frac{\gamma \cdot K_g \left(1 + \frac{b}{\sum \vec{\nabla} P_i} \right)}{\gamma_0 \cdot \mu_g} \sum \vec{\nabla} P_i \right) = k_D \cdot \left(MC_r - MC_v \right)$$
(42)

For dry atmospheric gasses the right-hand side can be assumed to be zero, but for moisture this represents the rate of vapourization of moisture from the resin.

Combining (41) with the parabolic sorption curve (24) and the definition of moisture content (23) leads to the equation describing how moisture content changes with time:

$$\frac{d}{dt}MC_r = -\frac{k_D}{\rho_{0dry}} \cdot \left(MC_r - k_1 \cdot \left(\frac{P_{H2O}}{P_{H2O}^*}\right)^2\right)$$
(43)

Finally, we assume the infiltration of resin into the fiber bed is described by Darcy's law

$$\overline{\nu}_{l} = \frac{d}{dt}\Delta z = -\frac{K_{l}}{\mu_{l}}\frac{\Delta P}{\Delta z}$$
(44)

where Δz is the distance that the resin front has penetrated into the fiber-bed. This distance is related to γ :

$$\Delta z = h_f \left(1 - \gamma \right) \tag{45}$$

Combining (52) and (53) gives the equation describing how γ changes with time

$$\frac{d\gamma}{dt} = -\frac{K_l}{\phi_{fiberbed} \cdot \mu_l} \frac{\left(P_{\infty} - \sum P_i\right)}{h_f^2 \cdot (1 - \gamma)}$$
(46)

Note that some details and manipulations of equations have been omitted to summarize the model derivation here. A detailed derivation of the equations being solved in the model and their implementation in MATLAB can be found in Appendix F and Appendix G respectively.

9.2 Model output

Example plots of the output of the MATLAB code are shown in Figure 9.3 to Figure 9.6. These example plots show a simulation of the debulk of a 0.3m long laminate that has initially equilibrated with a 75% relative humidity environment. The debulk time simulated is 24 hours. Note that because the dry gas is almost entirely removed within the first ten minutes, the plot of dry gas pressure has been inset with a plot showing only the first ten minutes of the simulation. The plot of moisture vapour pressure has also been inset with a plot showing only the first ten minutes to show features of this data that occur over this time scale.



Figure 9.3: Model output for dry gas pressure (with inset of initial ten minutes)



Figure 9.4: Model output for moisture vapour pressure (with inset of first ten minutes)



Figure 9.5: Model output for resin infiltration parameter



Figure 9.6: Model output for resin moisture content

Interpreting the above plots, they predict that over a 24 hour debulk of this part:

- Essentially all the dry gasses are quickly removed from the gas channels.
- At the vacuum edge the water vapour pressure is reduced to zero, and at the far end it is
 reduced by a factor of 10. Although this is removed just as quickly as the dry gasses, it is
 replaced by the vaporization of moisture dissolved in the resin. There is also a brief (~1 minute)
 initial dip in moisture vapour pressure (see Figure 9.4, inset) as moisture is quickly removed
 along with the dry gasses while the total gas pressure is still relatively high.
- The resin infiltration parameter is nearly uniform across the length of the part for all times, and has gone from an initial value of 0.1 to about 0.25. This can be interpreted as a reduction in porosity during the debulk to 83% of its initial value:

$$1 - 0.25 / 1 - 0.1 = 0.75 / 0.9 = 83\%$$
 (47)

• The resin moisture content has been reduced across the entire part, by about a factor of 10 at the breathing edge, and by about a factor of 5 at the far end.

9.3 Model Verification

The implementation of the MATLAB model was verified in several ways. A prototype finite-difference model was built in excel. This prototype model included gas flow with the Klinkenberg effect as well as resin infiltration, but did not include moisture diffusion. The output of this model was compared with the output of the MATLAB model when moisture was not present, and the models were able to produce the same results.

Additionally the model was run for trivial cases where its behavior can be easily predicted in advance. For example, if the initial pressure is set to half an atmosphere, the initial degree of impregnation is set close to zero, and the boundary conditions are that there is no gas flow at either edge (laminate is sealed) then we expect to see resin infiltration proceed and gas pressure simultaneously increase until gas pressure approaches one atmosphere and the degree of resin infiltration approaches 1/2. These are indeed the results of the model, shown in Figure 9.7.



Figure 9.7: Model output for validation

9.4 Comparison with Experimental Results

The predictions of the model can be directly compared with the results of the experiments in 5.6 that measured prepreg moisture content after the debulk step. Figure 9.8 superimposes the measurements and predictions for the average moisture content after varying debulk times. The model is able to predict these values reasonably well.



The profiles of the moisture content after debulk can also be compared (see Figure 9.9). Although the average moisture content values agree fairly well, the shape of the profiles does not agree well with the experimental measurements. The experimentally measured profiles are substantially flatter than the profiles predicted by the model.

136



Figure 9.9: Measured and predicted moisture content profiles after debulk based on baseline diffusion rate The parameters of the model were varied to see if a better fit to the experimental data could be achieved. All else being equal, flatter profiles are produced when the diffusion rate is slower. If the diffusion rate is decreased by a factor of 4 the shape of the model's predicted moisture content profiles compare quite well with the experimentally determined profiles. Figure 9.10 superimposes the model predictions for average moisture content after debulk using the lower diffusion rate parameter with the experimental data. With this change the moisture content profiles predicted by the model compare better with the experimental data. The average moisture content and moisture content profiles are shown in Figure 9.10 and Figure 9.11.



Figure 9.10: Measured and predicted moisture content with diffusion rate decreased



Figure 9.11: Measured and predicted moisture content profiles with diffusion rate decreased

It is encouraging that the model's predictions can be made to agree reasonably well with the experimental measurements by adjusting input parameters. This suggests that the poor agreement

between the model and the experiment when the baseline input parameters are used is not an indication that the model has failed to capture the most important physical mechanisms, but is mostly the result of variability in input parameters. The need to adjust input parameters here is not unexpected as the resin used in the experimental measurements of the diffusion coefficient was drawn from a different roll of material than the parts used in the porosity experiments, and it is known that different rolls of material can often differ substantially. The diffusion rate will be affected by factors such as differences in initial degree of resin impregnation, or by prepreg out time and initial degree of cure of the resin. The diffusion coefficient is strongly dependent on the degree of cure: the difference in diffusion coefficient between uncured and cured resin can be three to four orders of magnitude [25] [63] [73]. Additionally, the diffusion rate parameter here is estimated from tests made on neat resin rather than prepreg. As noted in section 5.5 the effective rate of diffusion through prepreg will depend on the arrangement of void spaces and fibers relative to the resin. Diffusion occurs very quickly through the void spaces, whereas the fibers are essentially impenetrable, so the presence of these phases will speed up or slow down, respectively, the effective rate of diffusion in prepreg relative to neat resin.

It is important to emphasize that here we are not trying to optimize the parameters but to show that the model is capable of predicting the experimental results given appropriate input parameters. This highlights the challenge that material variability presents to modelling the processing of prepreg into composite parts. Caution must be taken when assuming that a measured parameter from one sample of material can be applied to another piece of material.

9.5 Model Behavior

It is interesting to observe the behavior of the model as the process parameters are varied. In Figure 9.12 the effect of varying the permeability and diffusion coefficient on the moisture content during the debulk step is shown. The debulk time in each case has been selected to achieve the same final average

moisture content. The baseline permeability and diffusion rate parameters are the values from Table 9.3, and are each varied up and down by a factor of 4.

In the 0.3m parts the time scale for moisture diffusion and moisture vapour flow are similar, (see Figure 4.5). However, when the diffusion rate is decreased or the permeability increased the time scale required for diffusion becomes the limiting factor in removing moisture and the moisture content profiles become flatter. When the permeability is decreased or the diffusion coefficient increased the time scale for moisture vapour flow becomes limiting and the moisture content profiles become steeper. These effects can be seen as the permeability and diffusion rates are varied in Figure 9.12.

Decreasing either parameter also means that longer debulk times are required to remove the same amount of moisture.



Figure 9.12: Resin moisture content over a debulk when permeability and diffusion coefficient are varied

Simulations were run varying the diffusion rate and permeability parameters over an even larger range, and the time required to reach an equivalent moisture content was determined for each case. The results of these simulations are shown in Table 9.5. For each level of diffusion coefficient and permeability level, the time scale associated with that transport mechanism is also shown, as calculated using (11) and (12).

Debulk Times (h)		Diffusion Coefficient/ Time scale				
		6.25%	25%	100%	400%	1600%
Permeability / Ti	166.2 min	41.5 min	10.4 min	2.6 min	0.6 min	
25%	75.0 min	200	130	115	110	108
100%	18.7 min	125	40	24	23	22
400%	4.7 min	119	31	10	6	5.4
1600%	1.2 min	119	30	7.7	2.5	1.5
Baseline pe	$100\% = 1 \cdot 10^{-13} m^2$					
Baseline diffusion	$100\% = 2.6 \cdot 10^{-12} m^2 \cdot s$					

Table 9.5: Equivalent debulk time while varying permeability and diffusion coefficient

For debulk times that fall near the main diagonal in Table 9.5 the time scales for diffusion and moisture vapour flow are of similar magnitude, and varying either the permeability or diffusion coefficient has a substantial effect on the debulk time. The required debulk times near the upper right corner are dominated by the long time scale required for moisture vapour flow, and varying the diffusion coefficient here has little effect. Similarly, near the bottom left corner the time scale required for diffusion dominates and varying the permeability has little effect. (When available in colour these conditions are denoted by red and green respectively.) This demonstrates that the time scale calculations proposed in section 4.3 do produce useful indications of time scale for comparison of these transport mechanisms.

For debulk times near the lower right corner of Table 9.5 increasing both the permeability and diffusion coefficient by a factor of four also increases the required debulk time by a factor of four. Away from this

corner the debulk time is increased by somewhat more than a factor of four. This is because during a longer debulk resin infiltration will begin to close the vacuum channels and so the permeability decreases during the debulk. If either the permeability or diffusion coefficient are varied downward by *another* factor of four from the minimum values shown in Table 9.5 the average moisture content never reaches the baseline level because resin infiltration goes to completion and all gas flow stops before the target moisture content is reached. The time required for resin infiltration to complete at room temperature is about 475 hours (see Figure 4.8).

9.6 **Porosity Estimation**

It would be useful to compare the output of the model with the measured bulk porosity levels from the experiments in chapter 7; however, the model is only designed to simulate an isothermal debulk whereas the experiments measured the bulk porosity levels after the cure processing step. By making some simplifying assumptions about what occurs during the curing step a simple method is proposed for estimating the final (post-cure) part bulk porosity level from the parameters simulated by the model up to the end of the debulk (Figure 9.13).



Pressure in gas channels is equal to resin pressure. No resin movement. Pressure low in gas channels. Pressure Resin viscosity drops and resin quickly difference has caused some resin infiltration into gas channels.

infiltrates gas channels until pressures are equal again.

Figure 9.13: Resin movement during cure and debulk

To estimate the bulk porosity of the final cured parts using the values of these parameters at the end of

the debulk we assume:

- The flow of resin into the void spaces, quantified by β (or equivalently by γ), has already decreased the bulk porosity somewhat during the debulk.
- At the elevated temperatures involved during the cure step the resin's viscosity decreases by several orders of magnitude. We assume during this period the resin will flow until the internal gas pressure is equal to the external pressure. (In OOA processing this is approximately 1 atmosphere.)

The final bulk porosity is therefore given by:

$$\varphi = \varphi_0 \cdot \frac{1 - \beta}{1 - \beta_0} \cdot \frac{P_a + P_w}{P_\infty}$$
(48)

Unfortunately we cannot say in advance that we expect this estimate to be either higher or lower than the measured values because in making our simplifying assumptions we ignore both effects that act to

increase and to decrease the porosity. For example, during the cure cycle the vacuum system continues to remove gas from the laminate and so the real gas pressure in the vacuum channels during the cure will be lower than the post-debulk pressure predicted by the model. Because the laminate is heated during the cure, however, the vapourization of volatiles out of the resin will be accelerated and this will tend to increase gas pressure and hence porosity. Because we do not know which effect will dominate during the cure we do not know a priori if this estimate will be conservative or not.

9.6.1 Comparison to Experimental Results: Average Porosity

The model was used to simulate a debulk using parameters matched to the parameters varied in the experiments discussed in chapter 6. The spatially averaged value of β , P_a , and P_w was taken at the end of the simulated debulk and these were fed into (48) to give an estimated bulk porosity value. The reduced (25%) diffusion rate discussed in section 9.4 is used here.

The estimated and experimentally measured porosity values for laminates exposed to 75% and 33% relative humidity are compared in Figure 9.14 and Figure 9.15 respectively.



Figure 9.14: Comparison of estimated and measured bulk porosity levels for laminates exposed to 75% relative humidity



Figure 9.15: Comparison of estimated and measured bulk porosity levels for laminates exposed to 33% relative humidity

In most cases the estimated bulk porosity level is within a factor of 2 to 3 of the measured bulk porosity level. Additionally, many of the bulk porosity measurements are under-estimated by the model by around 0.5%. This effect is discussed further in section 9.6.3 below.

Notably the bulk porosity of the 1m long parts that were debulked for only 0.5hr are not underestimated but rather over-estimated by the model. This is consistent with other departures we observe between the model and experiments, and can be attributed to the effect of the simplifying assumptions made in the model regarding the way resin infiltration proceeds with time, and its influence on permeability. (For further discussion of this see section 11.1.)

9.6.2 Comparison to Experimental Results: Porosity Profiles

The bulk porosity profiles estimated by the model can also be compared with those measured in experiments. This comparison is shown in Figure 9.16 to Figure 9.19 below.



Figure 9.16: Comparison of estimated and measured bulk porosity profiles, 1m parts exposed to 75% relative humidity



Figure 9.17: Comparison of estimated and measured bulk porosity profiles, 1m parts exposed to 33% relative humidity



Figure 9.18: Comparison of estimated and measured bulk porosity profiles, 0.3m parts exposed to 75% relative humidity





We can see similar features in the porosity profiles, especially the tendency of equation (48) to underestimate the porosity by about 0.5%. In the 1m parts especially we can also see that even in cases where the average porosity is poorly estimated by the model, the shape of the porosity profile is approximately correct.

9.6.3 Disconnected Void Component Porosity Estimation Model

A relatively consistent feature of the porosity estimation model (48) is a tendency to under-estimate bulk porosity levels by around 0.5%. This supports the idea, previously observed by Farhang [9], that a small component of the bulk porosity is contributed by resin voids - bubbles contained entirely within the resin and disconnected from the interconnected network of gas channels - and that because it is disconnected this component persists through the debulk and cure. This idea is also consistent with the observation (see 7.5.3) that as surface porosity approaches zero, the bulk porosity approaches a value around 0.5%, which could also be explained by a persistent component of the total bulk porosity constituted by disconnected resin voids.

This suggests a simple improvement that can be made to the porosity estimation model. We assume that the assumptions outlined above in section 9.6 provide reasonable estimates of the porosity resulting from the interconnected network of voids, but further assume there is some component of porosity resulting from disconnected resin voids. These are not evacuated during debulk and are therefore not infiltrated by resin during the cure cycle. Modifying equation (48) to treat the two void components separately gives an improved "disconnected void component" or *DVC* porosity estimation model:

$$\varphi = (\varphi_0 - \varphi_d) \cdot \frac{1 - \beta}{1 - \beta_0} \cdot \frac{P_a + P_w}{P_\infty} + \varphi_d \tag{49}$$

Here φ_d represents the porosity resulting from the disconnected voids and $(\varphi_0 - \varphi_d)$ represents the initial porosity resulting from the interconnected component of voids. Note that when φ_0 is much greater than φ_d then $(\varphi_0 - \varphi_d) \approx \varphi_0$ and equation (49) can be approximated as a vertical offset of φ_d from equation (48). For the MTM45-1 the prepreg used here this is the case with $\varphi_0 = 35\%$ and $\varphi_d = 0.5\%$.

Applying this improved model to the data presented above does yield an improvement in agreement between the estimated porosity and the experimentally measured porosity at most data points. Figure 9.14 and Figure 9.18 are reproduced below as Figure 9.20 and Figure 9.21 Fig# using the DVC estimation model (49) and provide examples of the improved agreement.



Figure 9.20: Improved porosity estimates using DVC model for laminates exposed to 75% relative humidity



9.6.4 Discussion of Porosity Estimation Models

Although the model does predict the resin moisture content after the debulk step, there was no discernible correlation observed between this predicted quantity and the porosity level measured in the experiments conducted. It is expected that higher levels of dissolved moisture remaining in the resin after the debulk should tend to increase the porosity level of the final parts, but this effect was not discernible in the present data set.

Using the improved DVC porosity estimation model the agreement between the estimate and the experiment is remarkably good and the majority of data points do show good agreement using this model. Although it is clear that certain points in the current data set are still not well estimated by the model, this is expected given the level of variability in the experimental data set.

Overall, considering the simplifying assumptions made in the model its ability to estimate porosity levels is encouraging. If further improvements can be made to our understanding of the underlying physical mechanisms, especially the evolution of porosity during the cure processing step, this type of modelling holds some promise.

9.7 Small Laminates and Resin Bleed

The porosity estimation model was not compared to the experimental data for the 0.1m laminates because the experimental results for these laminates involved a phenomenon outside the scope of this model, namely resin bleed and the corresponding reduction in resin pressure. If a future version of the model can be extended to simulate the effect of resin bleed and the corresponding decrease in resin pressure then it would be interesting to compare the model's results with this data. Currently the model is not able to do this. Nevertheless, the numerical model can help to explain some aspects of the bulk porosity data for the 0.1m laminates.

Evidence from areal density calculations (see section 7.5.4.2) suggests that a substantial amount of resin bleed is to blame for the elevated porosity levels seen in the 0.1m parts. It is hypothesized that resin bleed caused inadequate resin volume fraction in the laminate, and so more of the compaction pressure from the vacuum bag was transferred from the resin to the fiber bed. The resin pressure is decreased accordingly, which encourages void growth from moisture dissolved in the resin.

According to the model, for parts of this small size the post-debulk dry gas pressure is negligible after even the shortest debulk times (0.5hr), and equation (48) predicts a bulk porosity level of 0.1% or less. We therefore expect any porosity present to be caused by moisture remaining in the resin after the debulk step. The measured bulk porosity levels of the 0.1m laminates are shown in Table 9.6 along with the post-debulk moisture content of the laminate predicted by the model. Additionally, the final column shows the vapour pressure that this remaining moisture will have at the cure temperature of 120°C. This is calculated by using (29) to determine the value of k_1 at 120°C, then using Kardos' sorption curve (24) to calculate relative humidity from the moisture content. The saturated vapour pressure of water at 120°C is around 190 kPa, and the vapour pressure of the absorbed moisture can be calculated using the definition of relative humidity (78).

Relative Humidity Exposure	Debulk Time (h)	Measured Bulk Porosity Level	Post-debulk Resin Moisture Content	Vapour Pressure of Dissolved Moisture at 120 ^o C Cure Temperature (atm)
75%	0.5	4.84%	0.28%	0.73
75%	4	3.62%	0.0053%	0.10
75%	24	1.01%	0	0
33%	0.5	3.53%	0.042%	0.28
33%	4	0.41%	0	0
33%	24	0.52%	0	0

Table 9.6: Porosity in 0.1m laminates

Comparing this simulation with the experimental results, we see that laminates where the resin wasn't completely dried during the debulk may have suffered from the lack of resin pressure as they have bulk porosity levels much higher than otherwise expected. The laminates that were completely dried by the debulk have low bulk porosity levels of around 1% or less as the model would predict, and appear not to have suffered from the decreased resin pressure.

9.8 Limitations and Future Improvements

This model has shown that the approach of modelling the debulk step of OOA processing as interacting transport mechanisms can successfully predict the results of experiments. This is a step toward the goal of predicting porosity by directly modelling the most important phenomena involved in the OOA prepreg process. The present model is limited to the isothermal case, but it is hoped that future work will extend its scope through the cure cycle. This will require building a better understanding of some details of the void evolution process during the cure step that are not currently fully understood.

Future work should focus on extending the model's capabilities to the non-isothermal conditions of the cure step and on understanding the evolution of voids that occurs during the cure. In particular an ability to predict how porosity levels will be affected during the cure when there are elevated moisture contents in the resin will help move towards the goal of a robust predictive capability for porosity.

10 Processing Strategies

It is expected that the understanding of OOA processing presented above will be useful in developing new OOA prepreg manufacturing processes and in understanding and troubleshooting existing ones. Two examples are provided below to illustrate how this understanding might help to inspire solutions to manufacturing problems and to provide insight into existing processes.

10.1 Dry Gas Flush

For a prepreg with a high moisture content the material must be dried before it is cured to avoid high porosity levels. Depending on the size of a part and its target moisture content, removing moisture during the debulk step can require extremely long time scales, and may even be impossible if the moisture removal time scales exceed resin infiltration time scales (see section 9.5).

The long times required are partially due to the low pressures available to drive gas flow in the late stages of the debulk. Once the dry atmospheric gasses have been removed the vapour pressure of dissolved moisture is the only driving force for the flow of moisture vapour to the vacuum system. This suggests that one strategy for processing prepregs where moisture content is a problem could be to somehow increase this driving force.

A strategy that could achieve this is suggested by the present understanding of the OOA prepreg process. If during the debulk step the end of the laminate farthest from the vacuum system were vented, then larger gas pressure gradients would be maintained across the laminate. It must be ensured that the air entering the vent is thoroughly dried to prevent this from *introducing* moisture to the laminate rather than removing it. The flushing of dry gas through the laminate would then maintain the pressure gradients necessary to quickly transport moisture out of the laminate. This idea can be simulated using the MATLAB code discussed in Chapter 9 by changing the boundary conditions. Here, a simulation of a 0.3m laminate that was exposed to 75% relative humidity is simulated as in Chapter 9 except that the dry gas pressure at the end of the laminate farthest from the breathing end is set to 1atm, and the water vapour pressure there is set to zero. A simulation using the same gas baseline permeability used in Chapter 9 is shown in Figure 10.1 along with a simulation assuming higher gas permeability. This high permeability condition may better reflect the true permeability of the material during a dry gas flush because a high internal gas channel pressure is maintained and this is known to lead to higher permeability levels because the gas channels are kept more open. Farhang [9] measured permeability levels as high as $6.9 \cdot 10^{-13}m^2$ when one side of the vacuum bag was continuously vented to atmosphere. A permeability value of $5 \cdot 10^{-13}m^2$ is used in the *increased permeability* simulation. The predicted moisture content over such a dry gas flush is shown in Figure 10.1. The moisture content over a simulated ordinary debulk is also shown for comparison.



Figure 10.1: Simulated Dry Gas Flush

An experiment using this strategy was also performed to compare this ability of this strategy to quickly remove moisture from a laminate to an ordinary debulk. The vacuum bagging arrangement is shown in Figure 10.2. The right hand side of the image shows the vacuum port and this end of the laminate is vacuum bagged normally. The opposite end of the vacuum bag is vented through a vinyl tube that pierces the vacuum bag. The tube is filled with silica gel desiccant to ensure the incoming air is thoroughly dried. Breather cloth ensures good air flow between the vent and the end of the laminate farthest from the vacuum system.



Figure 10.2: Vacuum bag arrangement for dry gas flush experiment

Two such laminates were produced and placed under a vacuum bag of this arrangement for 10 and 30 minutes respectively. The parts were 4 ply, 300mm long MTM45-1/5HS laminates, identical to the parts from the experiments described in chapter 7. The laminates were subsequently weighed, desiccated, and re-weighed to determine the moisture content as described in 7.4.2.1.

The amount of absorbed moisture removed by the *dry gas flush* method is shown in Figure 10.3 and compared with the fraction of absorbed moisture removed by an ordinary debulk (dashed lines). The results of the numerical simulations of these are also shown (solid lines). (The increased permeability case is used here.)



This strategy does indeed remove moisture much more quickly than an ordinary debulk. After a 30 minute dry gas flush nearly as much moisture was removed as during an 8 hour debulk.

The model is able to predict the effect of this processing strategy on the moisture content during the debulk processing step. Although in both cases the model shows a tendency to underpredict the moisture removal in the early part of the procedure, the deviations between the experiment and the model are similar for both cases.

This is one example of a processing strategy suggested by the present understanding of the OOA prepreg process, and demonstrates that the *transport mechanisms framework* proposed in this work is able to capture the important phenomena occurring during the processing of prepreg. It is the hope that process engineers will be able to use this understanding to discover other creative solutions to processing challenges in the future.

10.2 Heated Debulk

Long debulk times such as the 24 hour debulks discussed in the present work and elsewhere in the academic literature are often not feasible for manufacturing because of the extremely long cycle times required to produce parts. One strategy that has been suggested for decreasing this time is to perform the debulk at a temperature above ambient (though still below the cure temperature). This may be able to reduce the debulk time required because the vapour pressure of dissolved moisture is the driving force for moisture vapour flow, and this is strongly dependent on temperature. Diffusion also occurs more quickly at increased temperatures.

A very recent paper by Ridgard [74] discusses the use of "super-ambient temperature dwells" essentially a debulk above room temperature - to achieve shorter processing times and this paper has attracted considerable attention. (Heated debulks are not an entirely new idea. They have been used in industry for some time, and are even mentioned in patents as far back as 2000 [75], but there is little academic literature on the subject until recently.) The paper discusses results achieved using Cytec 5320-1/8HS, a very similar prepreg to the one used in the model and experiments discussed here. It was found that debulks around 50°C to 60°C were able to achieve in just four hours equivalent results to a 16 hour debulk at room temperature. It also found that temperatures above this range were less effective at producing a high quality part, and speculated that this was due to decreased resin viscosity which allowed resin infiltration to occur quickly, closing off the gas channels prematurely. Since resin

161

infiltration will also occur more quickly at elevated temperatures, the removal of moisture depends on the diffusion and moisture vapour flow mechanisms having time to operate before resin infiltration closes off the gas channels.

The model discussed in Chapter 9 can be used to simulate the effect of varying the debulk temperature to gain insight into the effect of these elevated temperature debulks. Temperature will affect the physical mechanisms involved in the OOA prepreg process, most significantly in the following ways:

- Initial resin viscosity is decreased at higher temperatures
- The vapour pressure of dissolved moisture is increased at higher temperatures
- The viscosity of the flowing gasses is increased (slightly) at higher temperatures
- The diffusivity of moisture in the resin is increased at higher temperatures

These temperature effects can be accounted for in the model and time scale calculations:

- The initial viscosity of MTM45-1 resin is known as a function of temperature from process simulation software [45]. See Figure 4.6, equation (14).
- The vapour pressure of dissolved moisture (for a given resin moisture content) is obtained through the dependency of the parabolic sorption curve's parameter k1 on temperature. See Figure 5.5, Figure 5.6, Figure 5.7, equation (25).
- The viscosity of air and water vapour as a function of temperature can be obtained from literature sources [76], [77]. This temperature dependency can often be ignored as the gas viscosities vary by no more than about 25% over the entire range 0°C to 100°C.
- The diffusivity as a function of temperature can be estimated using the Stokes-Einstein equation below (50) which states that the diffusivity in a liquid is approximately proportional to the temperature to viscosity ratio [78]:
$$D(T) = D_{T0} \left[\frac{T}{T_0} \cdot \frac{\mu_{T0}}{\mu_T} \right]$$
(50)

Here *T* is temperature, T_0 is a reference temperature, D_{T0} is the diffusion coefficient at the reference temperature, μ_T is the resin viscosity at a given temperature T, and μ_{T0} is the resin viscosity at the reference temperature T_0 . The resin viscosity as a function of temperature is given by equation (14). The diffusion parameter in the model kD is then calculated as shown in Appendix E.

These temperature effects can be applied to the time scale calculations made in section 4.3. We can now plot the time scales as a function of temperature as in Figure 10.4. The time scales that depend on part length have been plotted for several different part lengths.



Figure 10.4: Effect of Temperature on Time Scales

This plot shows that the time scale for dry gas flow is nearly independent of temperature, increasing very slightly at higher temperatures because of increasing air viscosity. The other processes are all accelerated at higher temperatures. This demonstrates the potential for reducing processing times by

performing a debulk at elevated temperatures, especially when moisture removal is necessary. The window of time before resin infiltration closes off the gas channels also decreases at higher temperatures.

By running the numerical model discussed in chapter 9 on a typical laminate we can determine the time required to remove 90% of the moisture from the resin. Figure 10.5 shows the result of two different runs of the model on 0.3m laminates exposed to 75% relative humidity. In the first case the resin viscosity has been set to an arbitrary high value $(10^{10}Pa \cdot s)$ to simulate the diffusion and gas flow processes alone without allowing any resin infiltration. The second case represents an ordinary model run with resin infiltration occurring normally.



Figure 10.5: Effect of Temperature of Moisture Removal

At lower temperatures the curves are essentially identical: the viscosity of the resin is very high and the case allowing resin infiltration is nearly identical to the case where there is no resin infiltration. At

increased temperatures these two curves begin to diverge as resin infiltration begins to close off the vacuum channels, slowing the moisture removal relative to the no-infiltration case where the channels remain completely open. At a temperature of about 65°C the gas channels close completely before a 90% reduction in resin moisture content is achieved and therefore this condition is never reached. In the case where the gas channels always remain completely open the time scales for moisture removal continue to decrease with increasing temperature.

These simulations are able to explain the observations of Ridgard that processing times can be reduced through the use of a heated debulk. Ridgard's observation that the results achieved by a 16 hour debulk at room temperature can be achieved in only 4 hours at a temperature of 60°C are very similar to what is shown in this simulation: that the result of a 20 hour debulk at room temperature can be achieved in less than 6 hours at 60°C. The simulation also reproduces and explains the effect that Ridgard observed regarding the use of even higher debulk temperatures, and supports his speculation as to the cause of this effect. At temperatures slightly above about 60°C the closing of the gas channels due to resin infiltration leads to longer processing times rather than shorter ones, and above 65°C further resin drying becomes impossible as the gas channels close completely.

The examples above demonstrate the utility of the numerical model to the process engineer. It is hoped that the model will become useful in suggesting new processing strategies, evaluating their effectiveness, and explaining the effects observed from their use.

165

11 Discussion

The framework presented in Chapter 4 is intended to provide an understanding of the interaction of different gas transport mechanisms in prepreg processing. The numerical model developed using this framework in Chapter 9 shows that the approach can predict and explain what is observed in experiments. The input parameters used in the model are intended to reflect reasonable estimates of the real values involved; however, optimizing these input parameters is not a goal here. Rather, the goal is to show that such a model can produce outputs that approximately agree with our experimental observations given uncertainty in input parameters.

11.1 Agreement between Model and Experiments

The approach of coupling moisture and gas transport has proven successful in predicting some of the important quantities involved in prepreg processing. For example, the model is able to predict post-debulk resin moisture contents as shown in Figure 9.10 and Figure 9.11. The transport mechanisms framework is also shown to be useful in suggesting novel processing strategies as solutions to processing challenges, and the model can predict the effect that these strategies will have on the process (section 10.1).

Because it is necessary to make approximations and simplifying assumptions in the model, the agreement between the model and experiments is not perfect. For example, a difference between the model and experiments is seen between the predicted and measured moisture content profiles (see Figure 9.8, Figure 9.10, Figure 10.1, Figure 10.3). The removal of moisture observed in the experiments is initially more rapid than in the model, and later becomes slower. This can be attributed to two simplifying assumptions made in the model:

Resin infiltration is modelled as a front of resin flowing into a static and homogeneous fiber bed.
 In reality, the process of resin infiltration is better thought of as occurring over two length and

time scales [79]. Initially resin flows relatively quickly into the larger spaces between fiber tows. Next, resin flows into the fiber tows themselves.

 The model assumes a direct proportionality between gas permeability and porosity. In reality, this relationship is non-linear and the permeability decreases faster than linearly as resin infiltration decreases the porosity. Additionally, the permeability goes to zero before the porosity does. Farhang [9] observed permeability approached zero in MTM45-1 prepreg when porosity reached about 5%.

When we compare the model's predictions with the experimental results we see:

- The porosity of the laminates exposed to high humidity levels and given short debulk times were overestimated by the model, where most other conditions were underestimated by the model.
- The experimental results show more rapid removal of moisture than the model predicts early in a debulk, and slower than the model predicts later.

The first point can be addressed by extending the current room temperature debulk model to the entire cure cycle. The second point suggests that a more refined moisture transport model would be required to achieve better agreement between the model and experiments. It is important to note that the degree of agreement between the model and experiments is also limited by uncertainty in the input parameters due to variability in the raw material. Refinements to the current model may not lead to a substantial improvement in predictions unless this uncertainty is also addressed.

11.2 Variability

A challenge in conducting repeatable experiments on prepreg materials is the variability of the materials and the process. There is substantial variability in the raw material, both between rolls of material and between different parts of the same roll. Parameters like permeability and initial degree of resin infiltration measured on one roll of material cannot be assumed to apply to a different roll of material, even if it is nominally the same product. The process is also difficult to control precisely, and even for an

167

experienced technician producing small flat parts under carefully controlled laboratory conditions there is variability in processing between different batches. Variability during processing is caused by several factors, many of which are difficult to detect or to anticipate. Variability in materials and in the process must be carefully considered when planning experiments. In the experiments discussed in Chapter 7 the range of processing parameters was carefully chosen based on preliminary experiments to produce laminates with a wide range of porosity levels. The prepreg used in the initial experiments was from a different roll of material than the final experiments, and there were differences between the rolls of material that affected the outcome of the experiments. For example, the gas permeability was substantially lower in the second roll of material, and the moisture sorption characteristics were also somewhat different. The effect this had on the experiment was that the porosity levels observed were reduced relative to what was expected. Many of the experimental parts had very low levels of porosity that made it more difficult to discern the relationships with process parameters that the experiment was intended to demonstrate. Future experiments could benefit if preliminary experiments and measurements of material properties could be conducted as much as possible using the same roll of material.

Finally, some variability is expected to be inherent in the manufacturing process itself. It was found that even producing small flat parts in a carefully controlled laboratory setting using the same equipment and the same experienced technician, there are often variations in the process that are substantial enough to cause parts to be rejected. It is expected that in an industrial operation where many different technicians are producing larger parts with complex geometry and using multiple pieces of equipment to do so, the variability in the process would be even greater.

Because of the challenges presented by variability in both the raw material and the process, achieving a robust predictive capability for porosity may ultimately require making the process itself more

168

predictable by addressing and reducing this variability. For example, it may be necessary for material manufacturers to achieve better uniformity in their product, and to reduce variability between material rolls (or even within one material roll). The OOA prepreg process could also be made more predictable by use of procedures and process equipment that minimizes variability in aspects of the process such as the layup and bagging, and the application of vacuum pressure to the laminate, and even the ambient temperature and humidity level in the facility.

11.3 Bulk and Surface Porosity

When comparing the measured levels of bulk and surface porosity, it is observed that the data sets both share minor features such as local peaks and valleys. This indicates several things:

- There is a relationship between bulk and surface porosity.
- Because these minor features are present in two independent data sets, we know that they are not due to measurement uncertainty but are actually physically present.
- The measurement techniques used are sensitive enough to resolve these small features.
- The porosity profiles are not smooth curves superimposed with measurement uncertainty. Rather, the porosity profiles themselves are not smooth curves.

Additionally, the surface porosity goes to zero when bulk porosity goes to about 0.5%, supporting the idea there is a small component of persistent bulk porosity constituted by resin voids that is difficult to remove during processing unless significant pressure can be applied to the resin (as in autoclave processing).

11.4 Generalization of Experimental Results

There are numerous factors that are known to influence process outcomes. This limits the extent to which we can comfortably generalize the findings of any one experiment to other materials and processes. Some caution should be taken when generalizing the findings of this work to different materials or processing configurations, such as:

- Different fibre architectures
- Different resin systems
- Different resin configurations such as partially impregnated vs fully impregnated prepregs, prepreg with a resin film on one-side versus resin film on both sides, or through-thickness breathing prepreg with resin in strips instead of films
- Different processing arrangements, such as tacky side against tool vs tacky side away from tool
- Net-resin processes versus processes where resin is bled
- Different cure cycles
- Different vacuum bagging consumables

12 Summary and Contributions

The experimental work and models presented above have expanded our understanding of the OOA prepreg process in several ways:

General knowledge:

- Established what are the most important mechanisms affecting the evolution of voids during the OOA prepreg process: gas flow, moisture diffusion, moisture desorption, and resin flow.
- Proposed a framework for applying our knowledge of these mechanisms to understand the void problem. This framework consists of a simplified prepreg microstructure and a description of how it evolves due to the action of the transport mechanisms above. This framework can be used to help visualize and reason about the microstructural changes that occur during prepreg processing.
- Established a thorough understanding of the interaction between prepreg and moisture, how it can be absorbed during handling, and how it can later be released during processing.
- Identified some of the challenges in conducting experimental work on OOA prepregs and how process problems can affect the process outcomes.
- Quantified some of the variability seen in a typical commercially available OOA prepreg, specifically variability in the thickness and moisture content of the raw material.
- Addressed how this variability can affect experimental results and how it affects our ability to accurately measure and model the prepreg and the physical processes occurring within it during the OOA prepreg process.
- Produced a large and carefully controlled experimental data set with enough rigor and repetitions to address the experimental challenges identified.

Model development:

- Produced a model that connects the important transport mechanisms together, allowing isothermal solutions of the multi-physics "void problem" during the debulk processing step.
- Validated the model by comparison with experimental measurements of prepreg moisture content during debulk.
- Demonstrated the ability of the model to generate estimates of porosity levels in cured parts with reasonable accuracy, and with little to no use of parameters fit to the experimental data.

The model developed is a useful tool for predicting and understanding the effects that variations in the process parameters will have, and for suggesting and evaluating new processing strategies. For example:

- The understanding provided by the model suggests that flowing dry air through a prepreg laminate may be able to accelerate the removal of moisture. The model predicted the effect this processing strategy would have, and the model's predictions were comparable to those measured by experiments carrying out the suggested processing strategy.
- The model explains experiments in the recent literature regarding the use of heated debulks to reduce processing times. The model is able to reproduce several of the outcomes observed in the experiments.

In particular, the model is useful not only because it can predict processing outcomes, but also because it provides a framework for understanding the mechanisms and causality involved, and insight into what the effects of proposed changes to a process will be. This model is expected to be useful moving forward by:

- Providing a foundation for the development of further models that extend the current model's capabilities (eg. Non-isothermal conditions) and integrate new mechanisms as we begin to build a robust understanding of them (eg. moisture-driven void growth during cure)
- To support future experimental work by allowing experimenters to select a range of parameters to achieve a targeted effect, or that will produce a desired range of processing outcomes.
- To aid in suggesting and evaluating novel processing strategies to address processing problems such as the presence of porosity, or to achieve processing goals such as reducing cycle times.
- To provide process engineers with a method of estimating the quality controls or process
 parameters necessary to achieve a desired porosity level. This can be used to help avoid porosity
 problems when developing new manufacturing processes, or to help troubleshoot existing
 manufacturing processed where porosity has been a problem.

13 Future Work

There are several avenues of research that would improve our understanding of the OOA prepreg process and the outcome of which can be expected to improve our ability to predict and model porosity evolution. In the present work several experiments were conducted and a model was suggested to explain and predict the results of the experiments. The model shows some promise for its ability to predict what occurs during the debulk processing step, but our understanding of the cure processing step is not yet complete enough to allow it to be directly modelled. A major goal of future work in this area should be extending the model to be able to simulate a cure cycle. The most significant gap in our knowledge that is currently preventing this is the lack of a detailed understanding of the evolution of voids during the cure step of the OOA prepreg process, and in particular its relationship with moisture dissolved in the resin. While we do know under what conditions voids will grow due to the vapourization of moisture, we do not yet have an experimentally validated model that is able to predict the rate of void growth or shrinkage during the cure cycle or the resulting increase or decrease of porosity. This is a key piece of the puzzle that would allow the model to be extended beyond the debulk step through the cure step, potentially allowing a model that can directly predict porosity levels.

Refinements to the model could also be made by the development of more accurate models of resin infiltration and its influence on permeability. Current resin infiltration models are not able to reproduce some details of the observed pattern of resin infiltration (see section 11.1.

Another useful activity would be to determine to how well the present work generalizes and to what extent it remains valid over changes in the process. For example, all the experimental work here was conducted on MTM45-1 prepreg, and it will be useful to know how well the knowledge gained from experiments on this material generalize to other prepreg systems. It would be enormously useful to repeat the experimental work presented in Chapter 7 using different prepreg systems, different cure cycles, or simply laminates of different thickness. If the relationship between surface and bulk porosity, scaling relationships, models, etc. developed remain valid over these changes in the process that would demonstrate the scope of their usefulness.

Finally, the extension of the present 1D model to a 2D case or to the full 3D case would allow the porosity of more complex structures to be predicted, as well as allowing through-thickness transport to be accounted for. Through-thickness gas transport is necessary to model laminates that include such features as cores and ply drops.

In addition to extending the model, further experimental work would be useful to help further validate the model. It was shown that the model could make reasonable predictions of resin moisture content after debulk without requiring any parameters fit to the data. Validation of the other quantities predicted by the model - dry gas pressure, moisture vapour pressure and degree of resin infiltration would provide greater confidence that the model is an accurate representation of the OOA prepreg process.

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Appendices

Appendix A - Nondimensionalization of Darcy's Law for Gas Flow

The one-dimensional case of Darcy's law for a compressible fluid can be expressed as follows [8]:

$$\phi \frac{\partial p}{\partial t} = \frac{K_x}{\mu} \frac{\partial}{\partial x} \left(p \frac{dp}{dx} \right)$$

Where K_x is the permeability, μ is dynamic viscosity, x is distance, t is time, and ϕ is the porosity. p is

the dependent variable, while x and t are independent variables. To nondimensionalize, let:

$$x = \xi \cdot L$$
$$t = \tau \cdot \frac{\phi \mu L^2}{K_x p_0}$$
$$p = p^* \cdot p_0$$

Here L is the length of the region the flow is occurring in. Then Darcy's law becomes:

$$\frac{\partial p^*}{\partial \tau} = \frac{\partial}{\partial \xi} \left(p^* \frac{dp^*}{d\xi} \right) = \left(\frac{dp^*}{d\xi} \right)^2 + p \frac{d^2 p^*}{d\xi^2}$$

In the case where a material has an initial pressure of p_0 everywhere and experiences a step change to zero at one or both boundary conditions a solution to the nondimensional Darcy's law, for the given boundary conditions was solved using the finite difference method, and is shown below in Figure A.1.



Figure A.1: Pressure profiles (nondimensionalized Darcy's law)

The fraction of gas remaining as a function of time is shown in Figure A.2.



Figure A.2: Fraction of gas remaining (nondimensionalized Darcy's law)

Appendix B - Nondimensionalization of Fick's Law

Fick's 2nd law in 1 dimension can be nondimensionalized as follows. Fick's 2nd law is:

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

Where D is the diffusion coefficient, x is distance, t is time, and ϕ is the concentration. ϕ is the dependent variable, while x and t are independent variables. To nondimensionalize, let:

$$x = \chi \cdot x_c$$
$$t = \tau \cdot t_c$$
$$\phi = \varphi \cdot \phi_c$$

Then Fick's law becomes:

$$\frac{\phi_c}{t_c}\frac{\partial\varphi}{\partial\tau} = D\frac{\phi_c}{x_c^2}\frac{\partial^2\varphi}{\partial\chi^2}$$

Dividing through by $D \frac{\phi_c}{{x_c}^2}$ we obtain:

$$\frac{x_c^2}{D \cdot t_c} \frac{\partial \varphi}{\partial \tau} = \frac{\partial^2 \varphi}{\partial \chi^2}$$

We define the characteristic units:

$$\frac{x_c^2}{D \cdot t_c} = 1$$

Then $x_c = \sqrt{D \cdot t_c}$ and $t_c = \frac{{x_c}^2}{D}$

The nondimensionalized version of Fick's law is obtained:

$$\frac{\partial \varphi}{\partial \tau} = \frac{\partial^2 \varphi}{\partial \chi^2}$$

A convenient scale to use is to define x_c as the length of the region that diffusion is occurring through, or half this length if the step change occurs at both ends (from symmetry):

$$x_c = L$$

or
$$2x_c = L (2 \text{ sided})$$

The characteristic time scale is therefore:

$$t_{c} = \frac{L^{2}}{D}$$

or
$$t_{c} = \frac{L^{2}}{4D} (2 \text{ sided})$$

In the case where a material has an initial concentration of ϕ_c everywhere and experiences a step change to zero at one or both boundary conditions a solution was solved using the finite difference method, and is shown below in Figure B.1.



Figure B.1: Concentration profiles (nondimensionalized Fick's law)

The fraction of solute remaining is shown in Figure B.2.



Figure B.2: Fraction of solute remaining (nondimensionalized Fick's law)

Appendix C - Nondimensionalization of Darcy's Law for Resin Flow

C.1 Assuming Constant Viscosity

The differential equation governing the infiltration of resin into a planar fiber bed is (95):

$$\frac{d\gamma}{dt} = -\frac{K_l}{\phi_{fiberbed} \cdot \mu_l} \frac{\left(P_{\infty} - \sum P_i\right)}{h_f^2 \cdot (1 - \gamma)}$$

 γ is the dependent variable, while t is the independent variable. To nondimensionalize, let:

$$t = \tau \cdot t_c$$

Note that γ is already non-dimensional. The differential equation becomes:

$$\frac{1}{t_c}\frac{d\gamma}{d\tau} = -\frac{K_l}{\phi_{fiberbed} \cdot \mu_l} \frac{\left(P_{\infty} - \sum P_i\right)}{h_f^2 \cdot (1 - \gamma)}$$

/

Here K_1 , μ_1 , h_f , $\phi_{fiber bed}$ are assumed to be constant. This is roughly true during a debulk except when temperature is changing or when the debulk occurs at a temperature high enough that cure is advancing substantially. Here $(P_{\infty} - \sum P_i)$ is the difference between the total internal gas channel pressure and the external pressure on the vacuum bag. Because dry atmospheric gasses are often removed quickly and the remaining pressure is small, this can often be assumed to be constant and equal to the atmospheric pressure on the vacuum bag P_{∞} . Under these assumptions we can combine these all into a single parameter:

Let
$$B = \frac{K_l \cdot (P_{\infty})}{\phi_{fiber \, bed} \cdot \mu_l \cdot {h_f}^2}$$

Then

$$\frac{1}{t_c}\frac{\partial\gamma}{\partial\tau} = -B \cdot \frac{1}{(1-\gamma)}$$

Rearranging we obtain:

$$\frac{\partial \gamma}{\partial \tau} = -B \cdot \frac{t_c}{\left(1 - \gamma\right)}$$

Next we define the characteristic units:

$$B \cdot t_c = \frac{1}{2}$$
 or $B = \frac{1}{2t_c}$ or $t_c = \frac{1}{2B}$

Then the nondimensionalized version of the equation is obtained:

$$\frac{\partial \gamma}{\partial \tau} = -\frac{1}{2 \cdot (1 - \gamma)}$$

The solution to this differential equation is

$$\gamma(\tau) = 1 - \sqrt{C + t + 1}$$

where C is determined by the initial value of γ :

$$\gamma(0) = \gamma_0 = 1 - \sqrt{C+1} \Longrightarrow C = \gamma_0^2 - 2\gamma_0$$

The convenience of defining $B \cdot t_c = \frac{1}{2}$ is now apparent: defined this way t_c is the time it takes for the resin to completely infiltrate the fiber bed when $\gamma_0 = 1$. For values of γ_0 greater than about 0.7 this is still accurate to within 10% (see Figure C.1):

$$t_{c} = \frac{\phi_{fiber\,bed} \cdot \mu_{l} \cdot {h_{f}}^{2}}{2 \cdot K_{l} \cdot P_{\infty}}$$



Figure C.1: Relationship between gamma and tau

C.2 Alternative (Flow Index) Approach

Rearranging (95) we see that it is a separable DE:

$$\frac{d\gamma}{dt}(1-\gamma) = -\frac{K_l}{\phi_{fiber \, bed} \cdot \mu_l} \frac{\left(P_{\infty} - \sum P_i\right)}{h_f^2}$$

This time we do not assume viscosity is constant, but both γ and viscosity are functions of time:

$$\frac{d\gamma(t)}{dt}(1-\gamma(t)) = -\frac{K_l}{\phi_{fiber \, bed} \cdot \mu_l(t)} \frac{\left(P_{\infty} - \sum P_i\right)}{h_f^2}$$

Integrating both sides with respect to time:

$$\gamma(t) - \frac{1}{2}\gamma(t)^{2} = \frac{K_{l}}{\phi_{fiber \, bed}} \frac{\left(P_{\infty} - \sum P_{i}\right)}{h_{f}^{2}} \cdot \int_{0}^{t} \frac{1}{\mu_{l}(t)} \cdot dt + C$$

Solving for γ :

$$\gamma(t) = 1 - \sqrt{2 \cdot \frac{K_l}{\phi_{fiber \, bed}}} \frac{\left(P_{\infty} - \sum P_i\right)}{h_f^2} \cdot \int_0^t \frac{1}{\mu_l(t)} \cdot dt + C$$

For initial condition $\gamma = 1$:

$$\gamma(t) = 1 - \sqrt{2 \cdot \frac{K_l}{\phi_{fiber \, bed}}} \frac{\left(P_{\infty} - \sum P_i\right)}{h_f^2} \cdot \int_0^t \frac{1}{\mu_l(t)} \cdot dt$$

Gamma reaches zero when:

$$\frac{K_{l}}{\phi_{fiber \, bed}} \frac{\left(P_{\infty} - \sum P_{i}\right)}{h_{f}^{2}} \cdot \int_{0}^{t} \frac{1}{\mu_{l}(t)} \cdot dt = 1/2$$

Define the flow index as:

$$\int_{0}^{t} \frac{1}{\mu_{l}(t)} \cdot dt$$

Then the flow index corresponding to complete resin infiltration is given by:

$$\int_{0}^{t} \frac{1}{\mu_{l}(t)} \cdot dt = \frac{\phi_{fiber\,bed} \cdot {h_{f}}^{2}}{2 \cdot K_{l} \cdot \left(P_{\infty} - \sum P_{i}\right)}$$

Appendix D - Fixed Point Humidity (FPH) Salt Solutions

Saturated salt solutions are useful for the control of relative humidity levels in closed containers. ASTM Standard E104 – 02 covers the practical aspects of this use. The humidity level in a closed container containing a saturated salt solution is a function only of the temperature and the salt used. A plot of FPH over a range of temeratures is plotted for various salts in Figure D.1. Data is drawn from [61] and [60].



Figure D.1: Fixed Point Humidity vs Temperature

Appendix E - Calculation of Input Parameters for Numerical Model

Areal weight of prepreg components:

Fibers	375	g/m²	UMECO Data Sheet (FAW=375 g/m ²)		
Resin	210	g/m²	UMECO Data Sheet (RW=36%)		
Total	585	g/m²	Fiber + Resin Areal Weights		

Component density:

Fibers	2000000	g/m³	Typical value for PAN Fibers	
Resin	1150000	g/m³	Cured resin density from data sheet minus ~3% due to cure shrinkage	

Region thickness contribution in uncured prepreg. Note that meaning of "thickness contribution" is volume per unit prepreg area, or equivalently areal weight/component density:

Total	0.000517	m	Measured average thickness of uncured prepreg	
Porous Region	0.000350	m	Measured from micrographs	
Resin Region	0.000167	m	Total thickness - contribution from porous region	

Component thickness contribution in uncured prepreg:

Fibers	0.0001875	m	Areal Wt/Density	
Resin	0.000182609	m	Areal Wt/Density	
Gas	0.000147049	m	Remaining Thickness	

Component volume fractions:

Fibers	36.26	%	Fiber thickness contribution/total thickness	
Resin	35.31	%	Resin thickness contribution/total thickness	
Gas	28.43	%	Gas thickness contribution/total thickness	

Region composition (in thickness contribution):

Nonporous	Resin	0.000167158	m	Defintion: nonporous region contains only resin
Region				
Porous	Fibers	0.0001875	m	Definition: All fibers are contained in porous region
Region	Resin	0.0000154507	m	Resin not contained in nonporous region
	Gas	0.000147049	m	Definition: All gas is contained in porous region

Required model parameters:

Gamma0	0.904918796	dimensionless	Definition: Gas fraction of porous volume not occupied by
			fibers (see Figure F.2)
phibed	0.464285714	dimensionless	Definition: Fraction of porous volume not occupied by
			fibers
rho0dry	1098367.347	g/m³	Density when gamma=0. Density=m/v. Mass is mass of
			fibers + mass of resin. V when gamma=0 is volume of
			porous region+volume of all resin.

Calculation of diffusion rate parameter :

The meaning of k_D is given by (76): $\dot{m} = k_D \cdot (MC_r - MC_v)$

The assumption is that the rate of transfer of moisture from deep within the resin to the interface between the resin and the gas channels can be modelled as a single element obeying Fick's law. Consider a representative volume element:



Figure E.1: Diffusion of moisture in resin film

Fick's law says:

$$J = -D \cdot \frac{\Delta \varphi}{\Delta x}$$

where J is the molar flux of moisture, D is the diffusion coefficient of moisture in the resin, and $\frac{\Delta \varphi}{\Delta x}$ is the concentration gradient. Since J is a molar flux, the mass flux is:

$$J \cdot M_{H2O} = -D \cdot M_{H2O} \cdot \frac{\Delta \varphi}{\Delta x}$$

where M_{H2O} is the molar mass of water.

Concentration is the number of moles per unit volume, and can be related to moisture content:

$$\varphi = \frac{n}{V} = \frac{m_{H2O} / M_{H2O}}{m_{resin} / \rho_{resin}} = MC \frac{\rho_{resin}}{M_{H2O}}$$

where m_{H2O} is the mass of absorbed water, M_{H2O} is the molar mass of water, m_{resin} is the mass of resin, ρ_{resin} is the density of the resin, and MC is the resin moisture content as defined in (20).

The concentration gradient can then be written in terms of moisture contents:

$$\frac{\Delta \varphi}{\Delta x} = \frac{\varphi_v - \varphi_r}{\Delta x} = \frac{\rho_{resin} \left(MC_v - MC_r \right)}{M_{H2O} \cdot \Delta x}$$

The molar flux in terms of moisture contents is therefore:

$$J \cdot M_{H2O} = -D \cdot M_{H2O} \cdot \frac{\rho_{resin} \left(MC_v - MC_r \right)}{M_{H2O} \cdot \Delta x} = D \cdot \frac{\rho_{resin} \left(MC_r - MC_v \right)}{\Delta x}$$

Because this is entering the gas channels from the resin films on either side, the mass rate of moisture vapourizing in the volume element under consideration is then:

$$2 \cdot J \cdot M_{H2O} \cdot A = 2 \cdot D \cdot A \cdot \frac{\rho_{resin} (MC_r - MC_v)}{\Delta x}$$

Dividing by the volume of the element gives us \dot{m} :

$$\dot{m} = \frac{2 \cdot J \cdot M_{H2O} \cdot A}{A \cdot t_{ply}} = \frac{2 \cdot D \cdot \rho_{resin} (MC_r - MC_v)}{\Delta x \cdot t_{ply}}$$

where t_{ply} is the initial thickness of the prepreg. Then from the definition of k_D :

$$k_D = \frac{2 \cdot D \cdot \rho_{resin}}{\Delta x \cdot t_{ply}}$$

Our best estimates of these variables for MTM45-1/5HS prepreg is:

Value	Value	Source
n	$2(10^{-12}m^2)$	Measured
D	$2.6 \cdot 10^{}m^{-} \cdot s$	(see 5.5)
ρ_{resin}	1098 kg/m ³	Calculated above
٨	0.00	1/2 thickness of resin
ΔX	0.0911111	film calculated above
t _{ply}	0.52 <i>mm</i>	Calculated above

Table E.1: Input values for diffusion parameter calculation in MTM45-1/5HS prepreg

$$k_D = \frac{D \cdot \rho_{resin}}{\Delta x \cdot t_{ply}} = \frac{2 \cdot 2.6 \cdot 10^{-12} \, m^2 \, / \, s \cdot 1098 \, kg \, / \, m^3}{0.00009 \, m \cdot 0.00052 \, m} = 0.12 \frac{kg}{m^3 \cdot s}$$
Appendix F - Derivation of Numerical Model



We consider an element of prepreg represented below (Figure F.1).

Figure F.1: Representative Volume Element

At the most basic level our RVE consists of a porous region V_p , which has a constant volume, and a nonporous region V_n which has a time-varying volume. Intuitively, the porous volume is the fiber-bed region, along with any gas and resin within it. The porous volume contains all of the solid (fiber) phase and the gaseous (void space) phase, and possibly a portion of the liquid (resin) phase. The non-porous volume contains only the balance of the resin. Since the porous region's volume is constant, when the volume of gas in the porous region decreases the volume of resin in the porous region must increase correspondingly. In the equations describing the transport of gas through the porous network the representative volume element is treated as homogeneous, so the physical arrangement of the phases is not an important consideration. The physical arrangement of the phases is only important in defining the degree of resin infiltration.

The volume of the representative element, V, is the sum of the volume of fibers, resin and void space in the element:

$$V = V_s + V_l + V_\sigma \tag{51}$$

The total volume of resin and fibers contained in each element remains constant, but as the gas volume is reduced and resin flows from the nonporous region into the porous region to replace the void space, the element's total volume decreases. We define a parameter, γ , that describes the relative porosity. It is defined as the ratio of the volume of void space, V_g , to the volume of void space when the resin and fiber phases are completely separate, V_g .



Figure F.2: Physical meaning of parameter gamma

$$\gamma = \frac{V_g}{V_{gs}} \tag{52}$$

Intuitively, gamma is equal to one when the resin and fibers are completely separate, and approaches zero as resin infiltrates the fiber bundles and the volume of void space approaches zero.

The initial volume of void space, $\,V_{0g}$ is related to the initial value of gamma, $\,\gamma_{0}$, by:

$$V_{0g} = \gamma_0 \cdot V_{gs} \tag{53}$$

The initial volume of the element, V_0 , is given by:

$$V_0 = V_s + V_l + V_{0g} = V_s + V_l + \gamma_0 \cdot V_{gs}$$
(54)

The symbol ϕ is used for the volume fractions of each component. Volume fractions are expressed on the basis of the initial volume rather than on the basis of the changing volume:

$$\phi_{s} = \frac{V_{s}}{V_{0}} = \frac{V_{s}}{V_{s} + V_{l} + V_{0g}}$$
(55)

$$\phi_{l} = \frac{V_{l}}{V_{0}} = \frac{V_{l}}{V_{s} + V_{l} + V_{0g}}$$
(56)

$$\phi_{g} = \frac{V_{g}}{V_{0}} = \frac{\gamma \cdot V_{gs}}{V_{0}} = \frac{\frac{\gamma}{\gamma_{0}} \cdot V_{0g}}{V_{s} + V_{l} + V_{0g}}$$
(57)

Unlike volume fractions expressed on the basis of the real (time dependent) volume, these will add to one only when $\gamma = \gamma_0$ and $V_g = V_{0g}$:

$$\phi_{s} + \phi_{l} + \phi_{0g} = 1 = \phi_{s} + \phi_{l} + \frac{\gamma_{0}}{\gamma} \phi_{g}$$
(58)

When gamma is equal to one, the porous region contains all the fibers and all the gas, and the nonporous region contains all the resin. Because the volume of the porous region does not change, the volume of the porous region is independent of gamma and can always be calculated as

$$V_p = V_s + V_{gs}$$
 or $V_p = V_s \cdot \left(\frac{1}{1 - \phi_{fiber \, bed}}\right)$ (59)

where $\phi_{fiber \ bed}$ is the porosity of the *fiber bed region only* when $\gamma = 0$, or equivalently the proportion of the porous region not occupied by fibers.

The volume of the nonporous region always contains only resin, so its volume will be equal to the total amount of resin less the volume of resin in the porous region. Since the porous volume is assumed to remain constant, the volume of resin that has flowed into the porous region is equal to the volume of void space eliminated from the porous region relative to when the fibers and resin are completely separate. The volume of the nonporous region then is

$$V_n = V_l - V_{gs} \left(1 - \gamma \right) \tag{60}$$

If $\gamma = 1$ and the resin and fiber bed are completely separate, then the nonporous volume is equal to the volume of resin V_I . If resin infiltration goes to completion then the volume of the nonporous region is

$$V_n = V_l - V_{gs} \tag{61}$$

Note that it is assumed that the prepreg does actually contain a sufficient quantity of resin to infiltrate the fiber bed completely, ie. the volume of resin V_l is greater than or equal to the volume of void space in the fiber bed V_{gs} .

The continuity equations for the fibers and resin are respectively:

$$\frac{\partial}{\partial t} (\rho_s \cdot \phi_s) + \nabla \cdot (\rho_s \cdot \phi_s \cdot \vec{v}_s) = 0$$
(62)

$$\frac{\partial}{\partial t} (\rho_l \cdot \phi_l) + \nabla \cdot (\rho_l \cdot \phi_l \cdot \vec{v}_l) = 0$$
(63)

In this model we assume that there is no movement of fibers or resin between elements, so $v_s = 0$ and $v_i = 0$. The continuity equations for fibers and resin then become trivial, as the second term disappears and so the first term is simply equal to zero.

In general, the gas in the void space may contain multiple components that need to be separately accounted for, such as air and water vapor. Applying the continuity equation to a single component of the gas phase gives us:

$$\frac{\partial}{\partial t} \left(\rho_i \cdot \phi_g \right) + \nabla \cdot \left(\rho_i \cdot \phi_g \cdot \vec{v}_g \right) = \dot{m}_i \tag{64}$$

where ρ_i is the density of component i of the gas, \vec{v}_g is the gas velocity, \dot{m}_i is a source term - the mass of gas component i generated per unit of time per unit of volume. In general this gas could be generated by vaporization of the component out of solution in the resin or as a reaction byproduct.

It is usually most convenient to measure the intensive quantities in this equation on the basis of the initial volume. We use the term "superficial" to refer to quantities when they are measured on this basis.

The terms in (64) have dimension of mass per unit volume per unit time. Since ρ_i is the true density of the component of the gas, $\rho_i \cdot \phi_g$ is the "superficial density", or mass per unit of initial volume. Similarly, $\rho_i \cdot v_g$ is the gas mass flux, or the mass passing through a unit area *of void space* per unit of time. The term $\rho_i \cdot \phi_g \cdot v_g$ then is the "superficial mass flux", or the mass passing through a unit of *initial* area per unit of time. The right hand side, \dot{m}_i , must also have dimension of mass per unit volume per unit time. It is the superficial volume specific mass vaporization rate. Its physical meaning is the mass of component i vaporizing per unit of time per unit of *initial* volume. This mass is being transferred from the liquid phase to the gas phase.

The ideal gas law gives us:

$$\rho_i = \frac{P_i \cdot M_i}{R \cdot T} \tag{65}$$

where P_i is the partial pressure of component i of the gas, M_i is the molar mass of component i, R is the molar gas constant and T is temperature, which is assumed not to be a function of spatial coordinates.

Combining (64) and (65) gives:

$$\frac{\partial}{\partial t} \left(\frac{P_i \cdot M_i}{RT} \cdot \phi_g \right) + \nabla \cdot \left(\frac{P_i \cdot M_i}{RT} \cdot \phi_g \cdot \vec{v}_g \right) = \dot{m}_i$$
(66)

From Darcy's law:

$$\vec{\bar{v}}_g = -\frac{K_g}{\mu_g}\vec{\nabla}P \tag{67}$$

where \vec{v}_g is the superficial velocity, K_g is the permeability, μ_g is gas viscosity and $\vec{\nabla}P$ is the pressure gradient. In general K_g will depend on γ and μ_g will depend on T and the local composition of the gas.

From Dalton's law:

$$P = \sum P_i \tag{68}$$

where P is the total pressure. Differentiating both sides of (68) with respect to x, and using the linearity of the divergence operator:

$$\vec{\nabla}P = \vec{\nabla}\sum P_i = \sum \vec{\nabla}P_i \tag{69}$$

Combining (67) and (69) gives:

$$\vec{\bar{v}}_g = -\frac{K_g}{\mu_g} \sum \vec{\nabla} P_i$$
(70)

Using the relationship between superficial velocity, velocity and porosity:

$$\vec{\bar{v}}_g = \phi_g \cdot \vec{v}_g \tag{71}$$

Combining (70) and (71) gives:

$$\phi_g \cdot \vec{v}_g = -\frac{K_g}{\mu_g} \sum \vec{\nabla} P_i$$
(72)

Combining (66) and (72) gives:

$$\frac{\partial}{\partial t} \left(\frac{P_i \cdot M_i}{RT} \cdot \phi_g \right) - \nabla \cdot \left(\frac{P_i \cdot M_i}{RT} \cdot \frac{K_g}{\mu_g} \sum \vec{\nabla} P_i \right) = \dot{m}_i$$
(73)

Rearranging (57) we obtain the expression for ϕ_g in terms of γ and the initial gas volume fraction ϕ_{0g} :

$$\phi_g = \gamma \cdot \frac{V_{gs}}{V_0} = \frac{\gamma}{\gamma_0} \cdot \frac{V_{0g}}{V_0} = \frac{\gamma}{\gamma_0} \cdot \phi_{0g}$$
(74)

Combining (73) and (74) gives:

$$\frac{\partial}{\partial t} \left(\frac{P_i \cdot M_i}{RT} \cdot \frac{\gamma}{\gamma_0} \cdot \phi_{0g} \right) - \nabla \cdot \left(\frac{P_i \cdot M_i}{RT} \cdot \frac{K_g}{\mu_g} \sum \vec{\nabla} P_i \right) = \dot{m}_i$$
(75)

This equation is the most general form of the equation describing gas transport in the laminate. To complete the model we need to derive three more expressions:

- 1. The expression for \dot{m}_i .
- 2. The relationship between gas permeability K_g and $\gamma.$
- 3. The differential equation describing how γ gamma changes with time.

For gas components that are absorbed in negligible quantities, such as air, \dot{m}_i can be approximated as being equal to zero. For gas components that are absorbed in significant quantities, like moisture, we must derive an expression for \dot{m}_i .

Absorbed moisture is distributed throughout the resin. Some will be located close to the vacuum channels, and some farther from the channels. Here we model diffusion approximately by introducing a first order approximation to Fick's law. We assume all the moisture is located some average distance l_D from the vacuum channels deep within the resin, and imagine it is effectively diffusing from this location to the interface between the resin and the vacuum channels. As a simplified approximation to Fick's law we ignore diffusion transients and assume the rate of mass transport from deep within the resin to the interface between the resin and the vacuum channels is directly proportional to the difference in moisture content between the bulk resin and the resin adjacent to the vacuum channels:

$$\dot{m} \propto \left(MC_r - MC_v\right) \rightarrow \dot{m} = k_D \cdot \left(MC_r - MC_v\right) \tag{76}$$

Here MC_v is the moisture content of the resin adjacent to the vacuum channels, and MC_r is the average moisture content of the resin in the representative volume element. MC_r is a dependent

variable solved for in the model. The resin adjacent to the vacuum channels is assumed to remain in equilibrium with the gas in the vacuum channels, and so MC_{v} is calculated from the partial pressure of moisture using the sorption curve. Kardos' parabolic sorption curve model fits the experimental data well for MTM45-1 carbon fiber prepreg:

$$MC = k_1 \cdot RH^2 \tag{77}$$

Where k_1 is an experimentally determined parameter and RH is equilibrium relative humidity. The definition of relative humidity is:

$$RH = \frac{P_{H2O}}{P_{H2O}^{*}}$$
(78)

where P_{H2O}^{*} is the saturated vapor pressure of water at a given temperature.

Combining (77) and (78) gives:

$$MC = k_1 \cdot \left(\frac{P_{H2O}}{P_{H2O}^*}\right)^2$$
(79)

When the \dot{m} term is positive it represents moisture leaving the resin and entering the vacuum channels. As moisture leaves the resin MC_r decreases. Moisture content is defined as:

$$m_{H2O} = m_{dry} \cdot MC_r \tag{80}$$

where $m_{H_{2O}}$ is the mass of absorbed water and m_{dry} is the dry mass of the material that has absorbed it.

The dry mass of an element does not change over time, and is the product of the initial dry pre-preg density and the initial element volume.

$$m_{H2O} = \rho_{0_{dry}} \cdot V_0 \cdot MC_r \tag{81}$$

where $\rho_{\rm 0 dry}$ is the initial density of dry pre-preg.

Differentiating both sides of (28) gives:

$$\frac{d}{dt}m_{H2O} = \rho_{0dry} \cdot V_0 \cdot \frac{d}{dt}MC_r$$
(82)

Dividing both sides by the volume of the representative element makes the left hand side identical with $-\dot{m}$:

$$\frac{d}{dt}m_{H2O}\cdot\frac{1}{V_0} = -\dot{m} = \rho_{0dry}\cdot\frac{d}{dt}MC_r$$
(83)

Then combining (83) with (76) and (79) the equation that describes how resin moisture content changes with time is:

$$\frac{d}{dt}MC_r = -\frac{k_D}{\rho_{0dry}} \cdot \left(MC_r - k_1 \cdot \left(\frac{P_{H2O}}{P_{H2O}^*}\right)^2\right)$$
(84)

Combining (75), and (76) gives:

$$\frac{\partial}{\partial t} \left(\frac{P_i \cdot M_i}{RT} \cdot \frac{\gamma}{\gamma_0} \cdot \phi_{0g} \right) - \nabla \cdot \left(\frac{P_i \cdot M_i}{RT} \cdot \frac{K_g}{\mu_g} \sum \vec{\nabla} P_i \right) = k_D \cdot \left(MC_r - MC_v \right)$$
(85)

As resin impregnation occurs, the void space decreases in size and there is a corresponding decrease in the permeability of the material. To account for this we consider K_g to be a function of γ . We assume the effective reduction in permeability is proportional to the reduction in the area of the vacuum channels. From the definition of gamma, this area is reduced from the initial area by a factor of $\frac{\gamma}{\gamma_0}$:

$$K_{g} = \frac{\gamma}{\gamma_{0}} \cdot K_{g0}$$
(86)

where $K_{\rm g0}$ is the initial permeability.

Combining (85) and (86) gives:

$$\frac{\partial}{\partial t} \left(\frac{P_i \cdot M_i}{RT} \cdot \frac{\gamma}{\gamma_0} \cdot \phi_{0g} \right) - \nabla \cdot \left(\frac{P_i \cdot M_i}{RT} \cdot \frac{\gamma \cdot K_g}{\gamma_0 \cdot \mu_g} \sum \vec{\nabla} P_i \right) = k_D \cdot \left(MC_r - MC_v \right)$$
(87)

Finally we need the expression describing how γ changes with time. The geometric arrangement of the three phases is shown below (with symmetry about the midplane of the fiber bed):



Figure F.3: Resin infiltration in a representative volume element

We assume that the resin moving in the z direction to infiltrate the fiber bed can be described by Darcy's

law:

$$\overline{v}_{l} = -\frac{K_{l}}{\mu_{l}} \frac{\Delta P}{\Delta z}$$
(88)

where \bar{v}_l is the superficial velocity of the advancing resin, K_l is the through thickness permeability of the fiber bed, μ_l is the viscosity of the resin, and ΔP is the difference in pressure between the far field resin pressure P_{∞} and the gas pressure in the voids P, and Δz is the distance that the resin has infiltrated into the fiber bed.

From the relationship between velocity, superficial velocity and porosity:

$$\overline{v}_l = \phi_{fiber \ bed} \cdot v_l \tag{89}$$

Combining (88) and (89):

$$v_l = -\frac{K_l}{\phi_{fiber\,bed}} \cdot \mu_l \frac{\Delta P}{\Delta z}$$
(90)

The velocity of the resin is identically the rate of change of Δz with respect to time:

$$\frac{d}{dt}\Delta z = -\frac{K_l}{\phi_{fiber\,bed}} \cdot \mu_l \frac{(P - P_{\infty})}{\Delta z}$$
(91)

Also, γ is related to Δz :

$$\gamma = \frac{h_f - \Delta z}{h_f} = 1 - \frac{\Delta z}{h_f}$$
(92)

Rearranging (92) gives:

$$\Delta z = h_f \left(1 - \gamma \right) \tag{93}$$

Combining (91) and (93) gives:

,

.

$$\frac{d}{dt}\left(h_{f}\left(1-\gamma\right)\right) = -\frac{K_{l}}{\mu_{l}}\frac{\left(P-P_{\infty}\right)}{\phi_{fiber\,bed}\cdot h_{f}\left(1-\gamma\right)}$$
(94)

Expanding the left hand side, using (68) to eliminate ${\it P}$, and rearranging (94) gives:

$$\frac{d\gamma}{dt} = -\frac{K_l}{\phi_{fiberbed} \cdot \mu_l} \frac{\left(P_{\infty} - \sum P_i\right)}{h_f^2 \cdot (1 - \gamma)}$$
(95)

This is the final relationship required by the model.

Finally, there is one more correction. Darcy's law assumes a no-slip condition at the walls of a channel where the fluid velocity is zero, but for gasses at low pressures this condition is no longer valid and this has the effect of increasing the flow rate. This is known as the Klinkenberg effect.

The effective flow increase is typically modeled by the addition of a factor that increases the permeability:

$$K_{eff} = K \left(1 + \frac{b}{P} \right) \tag{96}$$

where b is the Klinkenberg parameter. The equation for gas transport (87) then becomes:

$$\frac{\partial}{\partial t} \left(\frac{P_i \cdot M_i}{RT} \cdot \frac{\gamma}{\gamma_0} \cdot \phi_{0g} \right) - \nabla \cdot \left(\frac{P_i \cdot M_i}{RT} \cdot \frac{\gamma \cdot K_g \left(1 + \frac{b}{\sum \vec{\nabla} P_i} \right)}{\gamma_0 \cdot \mu_g} \sum \vec{\nabla} P_i \right) = k_D \cdot \left(MC_r - MC_v \right)$$
(97)

Appendix G - Implementation of Numerical Model in MATLAB

The model described above has been implemented in MATLAB using the PDEPE differential equation solver. Besides the equations laws derived above, there are some practical considerations that have to be made in order to actually implement a code to solve our problem in software such as MATLAB.

Because of a singularity in (42) when γ is equal to 1 the infiltration parameter must have an initial value γ_0 that is less than one.

Additionally, resin infiltration cannot increase once all the void space is removed, and γ goes to zero. To ensure this we multiply the right hand side of (95) by a function $step(\gamma)$ that causes $\frac{d\gamma}{dt}$ to be set equal zero whenever γ is less than some small but nonzero value, γ_{lim} .

$$step(\gamma) = (1 - sign(\gamma_{lim} - \gamma))/2$$
(98)

This function is equal to one when γ is greater than γ_{lim} , and is equal to zero when γ is less than γ_{lim} . A value of $\gamma_{lim} = 5 \cdot 10^{-3}$ provides acceptable results. The differential equation describing γ now becomes:

$$\frac{d\gamma}{dt} = -\frac{K_l}{\phi_{fiberbed} \cdot \mu_l} \frac{\left(P_{\infty} - \sum P_i\right)}{h_f^2 \cdot (1 - \gamma)} \cdot step(\gamma)$$
(99)

To solve our system of coupled differential equations MATLAB's built in PDEPE feature is used. This requires that the equations be input in the following format.

$$C\left(x,t,u,\frac{du}{dx}\right)\cdot\frac{du}{dt} = x^{-m}\cdot\frac{d}{dx}\left(x^{m}\cdot F\left(x,t,u,\frac{du}{dx}\right)\right) + S\left(x,t,u,\frac{du}{dx}\right)$$
(100)

Here u is a column vector with entries corresponding to the dependent variables and C, F, and S are entered as column vectors with entries containing the functions describing the differential equations for each such variable.

Additionally, it requires initial conditions in the format

$$u = icfun(x) \tag{101}$$

and boundary conditions in the format

$$p(x,t,u)+q(x,t)\cdot F\left(x,t,u,\frac{du}{dx}\right)=0$$
(102)

In this implementation of our problem we simultaneously solve for four dependent variables, p_{air} ,

 $p_{_{H\,2O}}$, γ and $M\!C_r$ over one spatial coordinate and time.

For (45) we need significant manipulation to put it into the correct form. Since the model implementation is 1D, the divergence and gradient operators become derivatives. We also expand the expression inside the derivative operator on the left hand side:

$$\frac{\phi_{0g} \cdot M_i}{RT \cdot \gamma_0} \left(\frac{d\gamma}{dt} \cdot P_i + \gamma \cdot \frac{dP_i}{dt} \right) - \frac{d}{dx} \left(\frac{P_i \cdot M_i}{RT} \cdot \frac{\gamma \cdot K_g \left(1 + \frac{b}{\sum \vec{\nabla} P_i} \right)}{\gamma_0 \cdot \mu_g} \sum \frac{dP_i}{dx} \right) = k_D \cdot \left(MC_r - MC_v \right)$$
(103)

Since this equation cannot contain $\frac{d\gamma}{dt}$, we use (99) to eliminate this. We also use (79) to eliminate

 MC_{v} :

$$\frac{\phi_{0g} \cdot M_{i}}{RT \cdot \gamma_{0}} \left(\gamma \cdot \frac{dP_{i}}{dt} - \frac{K_{l}}{\phi_{fiber\,bed}} \cdot \mu_{l} \frac{\left(P_{\infty} - \sum P_{i}\right)}{h_{f}^{2} \cdot (1 - \gamma)} \cdot step(\gamma) \cdot P_{i} \right) - \frac{d}{dx} \left(\frac{P_{i} \cdot M_{i}}{RT} \cdot \frac{\gamma \cdot K_{g} \left(1 + \frac{b}{\sum \vec{\nabla} P_{i}}\right)}{\gamma_{0} \cdot \mu_{g}} \sum \frac{dP_{i}}{dx} \right)$$

$$= k_{D} \cdot \left(MC_{r} - k_{1} \cdot \left(\frac{P_{H2O}}{P_{H2O}^{*}}\right)^{2} \right)$$
(104)

Now grouping terms into the required format:

$$\left(\frac{\phi_{0g}\cdot M_{i}\cdot\gamma}{RT\cdot\gamma_{0}}\right)\frac{dP_{i}}{dt} = \frac{d}{dx}\left(\frac{P_{i}\cdot M_{i}}{RT}\cdot\frac{\gamma\cdot K_{g}\left(1+\frac{b}{\sum\vec{\nabla}P_{i}}\right)}{\gamma_{0}\cdot\mu_{g}}\sum\frac{dP_{i}}{dx}\right) + \left(k_{D}\cdot\left(MC_{r}-k_{1}\cdot\left(\frac{P_{H2O}}{P_{H2O}^{*}}\right)^{2}\right) + \frac{\phi_{0g}\cdot M_{i}}{RT\cdot\gamma_{0}}\frac{K_{l}}{\phi_{fiber\,bed}\cdot\mu_{l}}\frac{\left(P_{\infty}-\sum P_{i}\right)}{h_{f}^{2}\cdot(1-\gamma)}\cdot step(\gamma)\cdot P_{i}\right)$$

$$(105)$$

 \Rightarrow

$$C = \frac{\phi_{0g} \cdot M_i \cdot \gamma}{RT \cdot \gamma_0}$$

$$F = \frac{P_i \cdot M_i}{RT} \cdot \frac{\gamma \cdot K_g}{\gamma_0 \cdot \mu_g} \sum \frac{dP_i}{dx}$$

$$S = k_D \cdot \left(MC_r - k_1 \cdot \left(\frac{P_{H2O}}{P_{H2O}^*} \right)^2 \right) + \frac{\phi_{0g} \cdot M_i}{RT \cdot \gamma_0} \frac{K_l}{\phi_{fiber \, bed} \cdot \mu_l} \frac{\left(P_{\infty} - \sum P_i \right)}{h_f^2 \cdot (1 - \gamma)} \cdot step(\gamma) \cdot P_i$$

For gasses that aren't absorbed by the resin the equation is the same except that the \dot{m} term is zero:

$$\left(\frac{\phi_{0g} \cdot M_{i} \cdot \gamma}{RT \cdot \gamma_{0}}\right) \frac{dP_{i}}{dt} = \frac{d}{dx} \left(\frac{P_{i} \cdot M_{i}}{RT} \cdot \frac{\gamma \cdot K_{g} \left(1 + \frac{b}{\sum \vec{\nabla} P_{i}}\right)}{\gamma_{0} \cdot \mu_{g}} \sum \frac{dP_{i}}{dx}\right) + \left(\frac{\phi_{0g} \cdot M_{i}}{RT \cdot \gamma_{0}} \frac{K_{I}}{\phi_{fiber bed}} \cdot \frac{(P_{\infty} - \sum P_{i})}{h_{f}^{2} \cdot (1 - \gamma)} \cdot step(\gamma) \cdot P_{i}\right)$$
(106)

$$\Rightarrow$$

$$C = \frac{\phi_{0g} \cdot M_{i} \cdot \gamma}{RT \cdot \gamma_{0}}$$

$$F = \frac{P_{i} \cdot M_{i}}{RT} \cdot \frac{\gamma \cdot K_{g} \left(1 + \frac{b}{\sum \vec{\nabla} P_{i}}\right)}{\gamma_{0} \cdot \mu_{g}} \sum \frac{dP_{i}}{dx}$$

$$S = \frac{\phi_{0g} \cdot M_{i}}{RT \cdot \gamma_{0}} \frac{K_{l}}{\phi_{fiber \, bed} \cdot \mu_{l}} \frac{\left(P_{\infty} - \sum P_{i}\right)}{h_{f}^{2} \cdot (1 - \gamma)} \cdot step(\gamma) \cdot P_{i}$$

For (99) the equation is already in the correct format.

$$\Rightarrow$$

$$C = 1$$

$$F = 0$$

$$S = -\frac{K_{l}}{\phi_{fiber \ bed} \cdot \mu_{l}} \frac{\left(P_{\infty} - \sum P_{i}\right)}{h_{f}^{2} \cdot (1 - \gamma)} \cdot step(\gamma)$$

Finally, the equation describing how the moisture content of the resin changes with time, (84) is already in the correct format as well:

$$\frac{dMC_r}{dt} = -\frac{k_D}{\rho_{0dry}} \cdot \left(MC_r - k_1 \cdot \left(\frac{P_{H2O}}{P_{H2O}^*}\right)^2\right)$$
(107)

$$\Rightarrow$$

$$C = 1$$

$$F = 0$$

$$S = -\frac{k_D}{\rho_{0dry}} \cdot \left(MC_r - k_1 \cdot \left(\frac{P_{H2O}}{P_{H2O}^*}\right)^2\right)$$

Finally, μ_g is the viscosity of the mixture of gasses, and this is implemented in the MATLAB model as a mole-weighted average of component viscosities:

$$\mu_g = \frac{\mu_a \cdot P_a + \mu_w \cdot P_w}{P_a + P_w} \tag{108}$$

The component gas viscosities are assumed to be independent of pressure, which is valid over the range typically seen in OOA processing.

G.1 Initial Conditions

The initial conditions of the four dependent variables, P_{air} , P_{H2O} , γ and MC_r , are determined as follows in the MATLAB model:

The initial partial pressure of water vapour, P_{H2O} , is assumed to be in equilibrium with the initial moisture content, and so is given by the parabolic sorption curve (77). Rearranging to solve for MC, we get:

$$RH = \sqrt{\frac{MC}{k_1}} \tag{109}$$

Relative humidity is defined as the ratio of the partial pressure of water vapor to the vapour pressure of pure water at that temperature. The vapor pressure of pure water as a function of temperature is given by the Antoine Equation. Note that the MATLAB model first automatically converts the Kelvin temperature to Celsius. Over the range of interest, 0°C-100°C, the Antoine equation is [54]:

$$P_{H2O}^{*} = \frac{101300}{760} \cdot 10^{\wedge} \left(8.07131 - \frac{1730.63}{233.426 + T_{celsius}} \right)$$
(110)

The initial partial pressure of water vapour is the product of this pressure and RH:

$$P_{0w} = P_{H2O}^* \cdot RH \tag{111}$$

The initial partial pressure of air is the remaining pressure required to make the pressures sum to one atmosphere, therefore:

$$P_{0a} = P_{atm} - P_{0w}$$
(112)

where $P_{atm} = 101300 Pa$ (or the local atmospheric pressure).

The initial values of γ and MC_R are simply γ_0 and MC_0 , properties of the initial prepreg material that must be measured.

G.2 Boundary Conditions

The boundary conditions for the four dependent variables are determined as follows:

For the gas pressure components P_{air} and P_{H2O} we assume there is zero pressure at the vacuum edge. At the far edge there is zero flux (and equivalently no pressure gradient. In the required format:

Vacuum edge:Far edge:
$$P_{air} = 0$$
 $\frac{dP_{air}}{dx} = 0$ $\frac{dP_{H2O}}{dx} = 0$

Neither $\frac{d\gamma}{dt}$ nor $\frac{dMC_r}{dt}$ depend on time or spatial derivatives, so the boundary conditions are trivial.

In the format required by PDEPE (102) these boundary conditions become:

Left edge (breathing edge):

$$p_{left} = [P_{air}, P_{H2O}, 0, 0]$$
$$q_{left} = [0, 0, 1, 1]$$

Right edge:

$$p_{left} = [0,0,0,0]$$

 $q_{left} = [1,1,1,1]$

In MATLAB the relevant code is:

pl = [ul(1); ul(2); 0; 0]; ql = [0; 0; 1; 1]; pr = [0; 0; 0; 0]; qr = [1; 1; 1; 1];

Appendix H - MATLAB Code for Numerical Model

function ooa gas model

%This file implements the model developed by James Kay and described in his %PhD thesis. It models coupled gas flow and resin infiltration, with a %source term for moisture and diffusion. Air and water vapor are %tracked seperately. Elements change volume, and resin infiltration is the %planar case, not the cylindrical case.

```
Kg = 1e - 13;
                                    %Gas permeability (longitudinal) in m^2
Kl = 1e-15;
                                   %Liquid permeability (radial tow) in m^2
mua = 18.6e-6;
                                  %Air viscosity in Pa*s
muw = 9.9e-6; %Water vapor viscosity in Pa*s
mul = 23400; %Resin viscosity in Pa*s at temperature t0
phig = 0.35; %Initial void space volume fraction (porosity)
phibed = 0.46; %Porosity of fiber bed
hbedt = 0.00018; %Half thickness of fiber bed in m
p0 = 101300; %Initial pressure in Pa
gamma0 = 0.9;%Initial gas fraction of porous volumegammalim = 5e-3;%Lower limit on beta (to ensure stability)pinf = 101300;%Atmospheric pressure on vacuum bagk1h2o = 0.00558;%Parameter for parabolic sorption curveR = 8.314;%Molar gas constant in m^3*Pa/mol/K
                               %Molar gas constant in m<sup>-3</sup>*Pa/mol/k
%Molar mass of water in kg/mol
%Molar mass of dry air in kg/mol
%Density of dry pre-preg when gamma=1 in kg/m<sup>3</sup>
%Parameter for diffusion rate in kg/m<sup>3</sup>/s
mh2o = 0.018;
mair = 0.02897;
rho0dry = 1098;
kD = 0.12;
b = 13000;
                                   %Klinkenberg parameter in Pascals.
1 = 0.300;
                                  %Length of laminate in meters
mc0 = 0.00313875;%Initial moisture content mh2o/mdryt0 = 25+273.15;%Temperature in Kelvin
rh0 = rhmc(mc0,k1h2o); %Initial internal humidity
p0h2o=rh0*vpw(t0); %Initial partial pressure of water vapor
m = 0;
                                              %Cartesian coordinate system
x = linspace(0, sqrt(1), 61);
                                             %Create mesh from 0 to sqrt(1)
x = x.^{2};
                                              %Mesh is now 0-1 with smaller elements near x=0
t = linspace(0, sqrt(24*60*60), 100); %Time mesh, (automatically refined)
                                              %More output detail closer to t=0
t = t.^{2};
sol =
pdepe (m, @advandinfpde, @advandinfic, @advandinfbc, x, t, [], Kg, Kl, mua, muw, mul, phig
, phibed, hbedt, 1, p0, gamma0, gammalim, pinf, p0h2o, k1h2o, t0, R, mh2o, mair, rho0dry, kD
,mc0,b);
% Extract the solution components as u1, u2, u3, and u4.
u1 = sol(:,:,1);
u^2 = sol(:,:,2);
u3 = sol(:,:,3);
u4 = sol(:,:,4);
% Plot the dependent variables
```

```
figure
surf(x,t,u1.*step(u3,gammalim))
title('Dry gas pressure')
xlabel('Distance x')
ylabel('Time t')
figure
surf(x,t,u2.*step(u3,gammalim))
title('Water vapour pressure')
xlabel('Distance x')
ylabel('Time t')
figure
surf(x, t, 1-u3)
title('Degree of resin infiltration (Beta)')
xlabel('Distance x')
ylabel('Time t')
figure
surf(x,t,u4)
title('Resin moisture content(x,t)')
xlabel('Distance x')
ylabel('Time t')
%Optionally output results to a text file.
%csvwrite('output.csv',(u1));
end
∞ _____
function [rh]=rhmc(mc,k1h2o)
%Takes moisture content and the parameter for a parabolic sorption curve
%and returns the equilibrium relative humidity.
rh = sqrt(mc/k1h2o);
end
function [ph2o]=vpw(T)
%Takes Kelvin temperature as an argument and returns saturated vapor
%pressure of water at that temperature. Uses the Antoine equation, and
%coefficients that are valid in the range 0°C to 100°C.
TC=T-273.15;
               %Convert to Celsius.
ph2o = 101300/760*10^(8.07131-(1730.63)/(233.426+TC));
end
function [step]=step(gamma,gammalim)
%Step function to avoid singularities in beta DE.
step=(1-sign(gammalim-gamma))/2;
end
function [mug]=mug(mua,muw,pa,pw)
%Returns the mole weighted average of the viscosities of the two gas
%components.
mug=(mua*pa+muw*pw)/(pa+pw);
```

end

```
function [c, f, s] =
advandinfpde(x,t,u,DuDx,Kg,Kl,mua,muw,mul,phig,phibed,hbedt,l,p0,gamma0,gamma
lim,pinf,p0h2o,k1h2o,t0,R,mh2o,mair,rho0dry,kD,mc0,b)
c = [(phig*mair*u(3))/(R*t0*gamma0); (phig*mh2o*u(3))/(R*t0*gamma0); 1; 1];
f =
[(u(1)*mair)/(R*t0)*(u(3)*step(u(3),gammalim)*Kg*(1+b/(u(1)+u(2))))/(gamma0*m
ug(mua,muw,u(1),u(2)))*(DuDx(1)+DuDx(2));
(u(2)*mh2o)/(R*t0)*(u(3)*step(u(3),gammalim)*Kg*(1+(b/(u(1)+u(2)))))/(gamma0*
mug(mua,muw,u(1),u(2)))*(DuDx(1)+DuDx(2)); 0; 0];
s = [(phiq*mair)/(R*t0*qamma0)*(Kl)/(phibed*mul)*(pinf-u(1)-
u(2))/(hbedt<sup>2</sup>*(1-u(3)))*u(1)*step(u(3),gammalim); kD*(u(4)-
k1h2o*(u(2)/vpw(t0))^2)+(phig*mh2o)/(R*t0*gamma0)*(K1)/(phibed*mul)*(pinf-
u(1)-u(2))/(hbedt<sup>2</sup>*(1-u(3)))*u(2)*step(u(3),gammalim); -
Kl/(phibed*mul)*(pinf-u(1)-u(2))/(hbedt^2*(1-u(3)))*step(u(3),gammalim); -
kD/rho0dry*(u(4)-k1h2o*(u(2)/vpw(t0))^2)];
end
∞
function u0 =
advandinfic(x,Kg,Kl,mua,muw,mul,phig,phibed,hbedt,l,p0,gamma0,gammalim,pinf,p
0h2o,k1h2o,t0,R,mh2o,mair,rho0dry,kD,mc0,b)
u0 = [p0-p0h2o; p0h2o; gamma0; mc0];
end
%
function [pl,ql,pr,qr] =
advandinfbc(x1,u1,xr,ur,t,Kg,K1,mua,muw,mu1,phig,phibed,hbedt,1,p0,gamma0,gam
malim,pinf,p0h2o,k1h2o,t0,R,mh2o,mair,rho0dry,kD,mc0,b)
pl = [ul(1); ul(2); 0; 0]; %Boundary conditions, vacuum at one edge.
ql = [0; 0; 1; 1];
                           00
%pl = [0; 0; 0; 0];
                          %Boundary conditions, sealed edges.
%ql = [1; 1; 1; 1];
                          % (Comment out unused boundary condition.)
pr = [0; 0; 0; 0];
qr = [1; 1; 1; 1];
end
```

Appendix I - Diffusion of Moisture Through Air and Resin

It can be shown that moisture diffuses much more quickly across an air-filled void than through an epoxy medium. A realistic situation that could be encountered within an OOA prepreg laminate is as shown in Figure I.1. Moisture diffuses at 25°C from a region of resin where the moisture content is 0.4% to a region where it is 0.1%.



Figure I.1: Moisture diffusion through epoxy and air

The moisture flux can be determined using Fick's law (8):

$$J = -D\frac{\partial\phi}{\partial x}$$

The density of dry MTM45-1 prepreg is approximately $1100 kg/m^3$ so the molar concentration of

moisture at the top and bottom surface of the resin are:

$$\phi_{top} = 0.4\% \cdot (1100 kg/m^3) / (0.018 kg/mol) = 244 mol/m^3$$

$$\phi_{bottom} = 0.1\% \cdot (1100 kg/m^3) / (0.018 kg/mol) = 61 mol/m^3$$

The molar concentration of water vapour in the air can be determined from the Kardos sorption curve model and the ideal gas law. From the Kardos sorption curve model the relative humidity at the upper and lower interface of the air-filled void is:

$$RH_{top} = \sqrt{\frac{MC}{k_1}} = \sqrt{\frac{0.4\%}{0.00558}} = 85\%$$
$$RH_{bottom} = \sqrt{\frac{0.1\%}{0.00558}} = 42\%$$

The saturated vapour pressure of water at 25°C is 3167 Pa, so from the definition of relative humidity the partial pressures of water vapour are:

$$P_{top} = 3167Pa \cdot 85\% = 2681Pa$$

 $P_{bottom} = 3167Pa \cdot 85\% = 1341Pa$

The molar concentration can be determined from the ideal gas law:

$$\phi_{top} = \frac{n}{V} = \frac{P}{RT} = 1.08 mol/m^3$$
$$\phi_{bottom} = 0.54 mol/m^3$$

The flux of moisture can now be determined using Fick's law:

Diffusion	Concentration Gradient	Diffusion Coeficcient	Molar Flux
	mol/m ⁴	m^2/s	mol/m ² /s
through resin	1.83 · 10 ⁶	10 ⁻¹⁰	$2.9 \cdot 10^{-5}$
through air	$5.41 \cdot 10^{3}$	$2.5 \cdot 10^{-5}$	$1.4 \cdot 10^{-1}$

In this situation the moisture travels about 4600 times faster through air than through resin. For other

typical moisture content values this figure remains on the order of several thousand times faster in air

than in resin.