Experimental Study of the Pre-gelation Behaviour of Composite Prepreg

by

Caitlin Duffner

B.S., Linfield College, 2016

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF

THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF SCIENCE

in

THE FACULTY OF GRADUATE AND POSTDOCTORAL STUDIES

(Material Engineering)

THE UNIVERSITY OF BRITISH COLUMBIA

(Vancouver)

December 2019

© Caitlin Duffner, 2019

The following individuals certify that they have read, and recommend to the Faculty of Graduate and Postdoctoral Studies for acceptance, a thesis/dissertation entitled:

Err.	n amina antal	Ctuder	oftha	Dra colotion	Daharriann	of Com	monita Da	~ ~ ~ ~
- C/X	рептиентат	SILICIV	or me	Pre-geration	Бенауюнг	01.011	idosne pr	enreg
	permentan	Stady	or the	rie genation	Denavioai	01 0011		opres.

submitted by Caitlin May Duffner in partial fulfillment of the requirements for the degree of Master of Applied Science in Materials Engineering Examining Committee: Anoush Poursartip, Materials Engineering Supervisor Göran Fernlund, Materials Engineering Supervisory Committee Member Frank Ko, Materials Engineering Additional Examiner

Abstract

As the composite industry grows, the science base that supports the industry must also grow. In the past, most of the work done on thermoset composite prepreg systems have studied the post – gelation response, leaving the initial condition of the material relatively unexplored. The initial, or pre-gelation, state of the material is becoming increasingly relevant as the industry transitions to new manufacturing processes, mainly automatic fibre placement (AFP) and forming, that handles and manipulates the raw prepreg. Recent works investigating manufacturing defects in composite parts have shown a strong connection between the initial condition of the material and the final part quality. As research and industry shift to working with raw prepreg, it is time to re-examine the pre-gelation behaviour in order to improve processes in the future.

This work studies the pre-gelation behaviour of unidirectional Hexcel AS4/8552 prepreg through several novel test methods. The methods presented offer a different perspective into the behaviour of the material. Initially a microscopic perspective was taken, and SEM microscopy was used to characterize the initial morphology of a ply of prepreg. This study presents the significance of variations in morphology and the impact of capillary flow driven ply consolidation. Next, to evaluate the macroscopic behaviour of prepreg, a non-contact approach using Digital Image Correlation (DIC) was developed. This method was able to capture global and local strain responses in the prepreg throughout processing. Findings show that the pregelation response is not as simple as previously thought. The material experiences a strong consolidating force when heated due to the effects of surface tension. Further tests performed in this study attempt to make connections between local morphology, resin variations and local variations in strain. These tests used DIC, IR thermography, optical microscopy, and SEM.

New insights into prepreg conditions are gained by evaluating the common trends seen with this suite of testing. This work concludes that pre-gelation behaviour in prepreg is a highly complex state dependent on the variability of the material and the liquid-solid interfaces in the ply, as opposed to the traditional approach which considers the material response through a solid mechanics lens.

Lay Summary

One of the common methods for making composite parts is by laying up sheets of carbon fibres impregnated with a liquid resin. During processing the part is heated and the resin undergoes a chemical reaction that turns it from a liquid to a solid. This work examines the start of the process when the resin is a liquid. Several methods were developed to look at the physics that defines the liquid resins interaction with the fibres and how the whole composite behaves when heated. The primary research technique used to gather information on this behaviour was image analysis. The composite behaviour is clearly visualized and understood as a result of these experiments.

Preface

This thesis entitled "Experimental Study of the Pre-gelation Behaviour of Composite Prepreg" presents the research conducted by Caitlin Duffner under the supervision of Professor Anoush Poursartip and Dr. Navid Zobeiry at The University of British Columbia. All Chapters in this work were written by Caitlin Duffner under the supervision of Professor Anoush Poursartip.

The experimental work detailed in Chapter 3 Chapter 4 and Chapter 5 was designed and performed by Caitlin Duffner with the assistance of Dr. Navid Zobeiry who assisted with Digital Image Correlation work. All results were analyzed by Caitlin Duffner with the assistance of Dr. Navid Zobeiry and under the supervision of Professor Anoush Poursartip.

A version of the experimental results presented in Chapter 3 was used in a paper. Zobeiry, N., Duffner, C., "Measuring the negative pressure during processing of advanced composites" *Composite Structures*, 2018. The analysis for the paper was performed by Navid Zobeiry. Most of the experimental work by Caitlin Duffner.

A version of Chapter 3 and Chapter 4 was presented at the American Society for Composites Conference, Seattle, 2018. The presentation was given by Caitlin Duffner. A paper was published in the conference proceedings. Duffner, C, Zobeiry, N, Poursartip, A. "Examination of Pre-gelation Behavior in AS4/8552 Prepreg Composites" *American Society for Composites*, Seattle, 2018. Caitlin Duffner performed all the testing and analysis for this paper under the supervision of Professor Anoush Poursartip. The paper was written by Caitlin Duffner under the supervision of Professor Anoush Poursartip.

A version of Chapter 5 was presented at the Canadian International Conference on Composite Materials, Kelowna, 2019. A paper written by Caitlin Duffner under the supervision of Professor Anoush Poursartip was published in the conference proceedings. Duffner, C, Courteau-Godmaire, H, Zobeiry, N and Poursartip, A. "Characterization of Prepreg Initial Morphology". *Canadian International Conference on Composites,* Kelowna, 2019. The testing and analysis presented in this work were primarily done by Caitlin Duffner under the supervision of Anoush Poursartip. Results examining the void content was analyzed using a Matlab code developed by Hubert Courteau- Godmaire.

Table of Contents

Abstractiii
Lay Summaryiv
Prefacev
Table of Contents vii
List of Tables xi
List of Figuresxii
List of Supplementary Materialxviii
List of Symbols xix
List of Abbreviations xxi
Acknowledgements xxii
Dedication xxiv
Chapter 1: Introduction1
Chapter 2: Literature Review, Background, and Objectives5
2.1 Processing
2.1.1 Prepreg Fabrication
2.1.2 Carbon Fibre Fabrication
2.1.3 Prepreg Fabrication-Hot Melt Procedure
2.1.4 Thermoset Resin
2.1.4.1 Gelation
2.1.4.2 Glass Transition Temperature (Tg)
2.1.4.3 Vitrification
2.1.5 Free Strains Induced During Composite Processing
2.1.5.1 Thermal Expansion
2.1.5.2 Cure Development
2.2 Fluid Flow Through Porous Media
2.3 Surface Tension
2.4 Capillary Pressure
2.5 Darcy Flow
2.6 Initial Condition Effects on Defects
vii

2.6.1	Wrinkling	15
2.6.2	Porosity	15
2.6.3	Prepreg Tack	16
2.7 N	leasurement Techniques	17
2.7.1	Capillary-Type Dilatometers	17
2.7.2	Gravimetric Method	
2.7.3	Dynamic Mechanical Analysis (DMA)	
2.7.4	Thermomechanical Analysis (TMA)	19
2.7.5	Modified Rheology Method	
2.7.6	Fibre Bragg Grating	
2.7.7	Optical Methods	
2.7.	7.1 Digital Image Correlation (DIC)	
2.7.8	CTE and CS Literature Data	
2.8 R	esearch Objectives and Scope	
2.8.1	Synthesis of Literature	
2.8.2	Research Objectives and Scope	
2.8.3	Thesis Organization	
Chapter 3:	The Microstructural Response	
21 T.		
3.1 II	ntroduction	
3.1 If 3.2 N	ntroduction	31 31
3.1 If 3.2 N 3.2.1	ntroduction Iethod Material	31 31 31
3.1 If 3.2 N 3.2.1 3.2.2	ntroduction Iethod Material Pressure Conditions	31 31 31 32
3.1 II 3.2 M 3.2.1 3.2.2 3.2.2	ntroduction Iethod Material Pressure Conditions 2.1 Without External Pressure	
3.1 II 3.2 M 3.2.1 3.2.2 3.2.2 3.2.2	ntroduction Iethod Material Pressure Conditions 2.1 Without External Pressure 2.2 With External Pressure (1 atm)	
3.1 II 3.2 M 3.2.1 3.2.2 3.2.2 3.2.3	 htroduction Method Material Pressure Conditions 2.1 Without External Pressure 2.2 With External Pressure (1 atm) Sample Preparation and Test Set-Up 	
3.1 If 3.2 M 3.2.1 3.2.2 3.2.2 3.2.3 3.2.3 3.3 R	htroduction Method Material Pressure Conditions 2.1 Without External Pressure 2.2 With External Pressure (1 atm) Sample Preparation and Test Set-Up esults and Discussion	
3.1 If 3.2 M 3.2.1 3.2.2 3.2.3 3.2.3 3.2.3 3.3 R 3.4 S	ntroduction Iethod Material Pressure Conditions 2.1 Without External Pressure 2.2 With External Pressure (1 atm) Sample Preparation and Test Set-Up esults and Discussion ummary	
3.1 If 3.2 N 3.2.1 3.2.2 3.2.3 3.2.3 3.2.3 3.3 R 3.4 S Chapter 4:	ntroduction Iethod Material Pressure Conditions 2.1 Without External Pressure 2.2 With External Pressure (1 atm) Sample Preparation and Test Set-Up esults and Discussion ummary The Macrostructural Response	
3.1 If 3.2 N 3.2.1 3.2.2 3.2.3 3.2.3 3.2.3 3.3 R 3.4 S Chapter 4: 4.1 If	ntroduction Iethod Material Pressure Conditions 2.1 Without External Pressure 2.2 With External Pressure (1 atm) Sample Preparation and Test Set-Up esults and Discussion ummary The Macrostructural Response htroduction	
3.1 If 3.2 N 3.2.1 3.2.2 3.2.3 3.2.3 3.3 R 3.4 S Chapter 4: 4.1 If 4.2 D	htroduction Method Material Pressure Conditions 2.1 Without External Pressure 2.2 With External Pressure (1 atm) Sample Preparation and Test Set-Up esults and Discussion ummary The Macrostructural Response htroduction DIC Method	
3.1 If 3.2 N 3.2.1 3.2.2 3.2.3 3.2.3 3.2.3 3.3 R 3.4 S Chapter 4: 4.1 If 4.2 D 4.2.1	htroduction Method Material Pressure Conditions 2.1 Without External Pressure 2.2 With External Pressure (1 atm) Sample Preparation and Test Set-Up esults and Discussion ummary The Macrostructural Response htroduction DIC Method Material	

4.2.2	DIC Equipment and Calibration	44
4.2.3	Heating System	46
4.2.4	Sample Preparation	48
4.2.4	.1 Resin Sample	48
4.2.4	.2 Prepreg Sample	49
4.2.4	.3 Speckle Patterns	50
4.2.5	Image Processing and Acquisition	52
4.3 Re	esults and Discussion	52
4.3.1	Resin	52
4.3.1	.1 Summary of Resin Test Results and Discussion	59
4.3.2	Prepreg	60
4.3.2	2.1 Zone 5: Post-Gelation Thermal Response	64
4.3.2	2.2 Zone 4: Cure Shrinkage	66
4.3	3.2.2.1 Effect of Temperature on Cure Shrinkage	69
4.3.2	2.3 Zone 3: The Conflicting Effects of Thermal Expansion and Cure Shrinkage	e 70
4.3.2	2.4 Zone 2: Strain Drop	71
4.3.2	2.5 Zone 1: Initial Expansion	74
4.3.2	2.6 Pre-Condition	75
4.3	3.2.6.1 Step 1: Pre-Conditioning the Sample	83
4.3	3.2.6.2 Step 2: Main Cycle	84
4.3.2	DIC Strain Map Analysis	87
4.3	3.2.7.1 CTE Comparison Using DIC Strain Plot	89
4.4 Su	Immary of DIC Tests Results and Discussion	. 101
Chapter 5:	Variably in the Structure of a Ply	107
5.1 Int	troduction	. 107
5.2 M	ethods	. 107
5.2.1	Material	. 107
5.2.2	DIC Methods	. 107
5.2.3	SEM Methods	. 108
5.2.4	Infrared Thermography Methods	. 108
5.2.5	Optical Microscopy Methods	. 108

5.3 R	esults and Discussion	109
5.3.1	DIC	109
5.3.2	SEM	
5.3.3	Surface Characterization- Microscopy and IR Thermography	115
5.3.4	Summary of Results and Discussion	117
5.4 S	ummary of Macro Response	117
5.4.1	Pre-gelation effects	
5.4.2	Post-gelation	118
5.4.3	Strain and the Ply Morphology	119
5.4.4	Uncured Prepreg Surface Characterization	119
Chapter 6:	Conclusions, Contributions, and Future Work	121
6.1 S	ummary	121
6.2 C	onclusions	
6.3 F	uture Work	125
Bibliograp	hy	127
Appendice	S	135
Appendi	x A Critical Height of a Puddle	
A.1	Theory and Calculations	
A.2	Methods	137
A.3	Results	139
A.4	Discussion	
Appendi	x B Prepreg Ply Void Count Analysis	141
Appendi	x C Issues with Pre-Gelation TMA Measurements	
C.1	Method	
C.2	Results	144
C.3	Discussion	

List of Tables

Table 2.1 Summary of CTE Values Reported in the Literature for AS4/8552 and 8552	. 23
Table 2.2 Summary of cure shrinkage (CS) values reported in the literature for AS4/8552 and 8552.	. 26
Table 3.1 Temperatures and Viscosities for Saturation Tests	. 33
Table 3.2 Ply Thickness Comparisons-Percentage of Approximate Cure Ply Thickness	. 39
Table 4.1 Temperature Cycles for DIC Tests Designed To Gel on the Hold	. 47
Table 4.2 Comparison of Speckle Techniques Used To Determine the Best Method to Be Used In DIC Testing	ed . 51
Table 4.3 Behavioural Breakdown of Pre-Gelation Resin by Temperature Zone	. 59
Table 4.4 Direction 2 Linear Glassy CTE Results of DIC Prepreg Tests	. 65
Table 4.5 Linear Cure Shrinkage Coefficients for Temperature Cycle 1 of Prepreg	. 67
Table 4.6 Calculated Total Resin Volumetric Cure Shrinkage	. 69
Table 4.7 Direction 2 Linear Drop in Strain for Two Hold Cycle Tests	. 83
Table 4.8 Direction 2 Linear CTELiquid Taken From the First Cool Down Portion for Two Hold Cycles Tests	1 . 84
Table 4.9 Direction 2 Linear CTELiquid Taken From the Second Ramp Portion for Two Hold Cycles Tests	. 85
Table 4.10 Direction 2 Linear Coefficient of Cure Shrinkage of Prepreg for Two Hold Cycle 1	Гest . 86
Table 4.11 Direction 2 Linear CTE Glassy of Prepreg	. 87
Table 4.12 Summary of All DIC Prepreg Tests- Free Strain Analysis Breakdown	105
Table A.1 Approximate Interface and Resin Properties	137
Table A.2 Critical Height Test Sample Thicknesses Before and After Heating	139
Table C.3 Summary of Substrates Tested for TMA Tests	143
Table C.4 Summary of TMA Results Broken Down Into Zones	148

List of Figures

Figure 2.1	Schematic of unidirectional ply with a conventional coordinate system, direction 1 is parallel to the fibres, direction 2 is perpendicular to the fibres, and direction 3 is through the thickness of the ply
Figure 2.2	Process map indicates the cure and temperature dependence of each state resin goes through. Each state will result in a different material response, so understanding and defining each region becomes important when talking about materials thermal and curing behaviour. 7
Figure 2.3	Schematic of the transition at the gelation point due to crosslink formation. As this chemical reaction occurs viscoelastic liquid resin transitions to a solid. This transition is non-reversible. When links are formed the resin is no longer able to flow freely
Figure 2.4	Graphical representation of the coefficient of thermal expansion (CTE). The thermal expansion of the material can be quantified from change in length and temperature data. The change in length divided by the original length is the strain, so, to simplify the CTE expression the change in strain is divided by the change in temperature 10
Figure 2.5	Schematic of the expected behaviour of a thermoset polymer composite during processing adapted from literature[47]. Between a and b the resin is in the liquid stage and very low curing if any occurs. It is expected that thermal expansion dominates the materials behaviour during this period. Between b and c the resin is still in the liquid state however some curing has begun and there is a mixed response as the effect of cure shrinkage increases. Between c and d the temperature is held and the effects of cure are isolated. A large decrease in volume occurs. Form d to e the curing is assumed to have stopped and only thermal contraction is seen
Figure 2.6	Breakdown of different common characterization techniques for measuring dimensional changes in resin and composite material systems
Figure 2.7	⁷ Flow chart representation of the breakdown of this thesis. Two major paths to evaluate the pre-gelation behaviour of prepreg are taken, microstructure focused and macrostructure focus. Each discovery made helps uncover the cause of the observed CTE and CS behaviour
Figure 3.1	HexPly AS4 12K/8552 roll used in this work. Production details (date, batch, production location, etc.) are specified along with information on the fibre and resin (areal weight, tow bundles details, and resin-fibre volume fraction)
Figure 3.2	Schematic of SEM conditions experiment. Two cases are shown, the first prepreg sits on a tool, the second vacuum bagging is added, and the vacuum is applied
Figure 3.3	One-ply of AS4/8552 prepreg at room temperature. Comparison of regions of high resin content (a) and dry fibre bed area (b). In (a) the prepreg appears to be fully saturated with resin. In Contrast (B) shows a section of the ply where resin has only saturated the top and bottom leaving dry fibres in and a large void in the center of the ply. These inconsistencies in resin saturation are seen through the prepreg

Figure 3.4	SEM images of cross-sectioned AS4/8552 prepreg samples. The controlled case. No elevated temperate or vacuum pressure was applied
Figure 3.5	SEM images of cross-sectioned AS4/8552 prepreg samples. For condition one, no pressure was applied during heating: (a) one ply of prepreg held for 15 minutes at 40°C (b) one ply of prepreg held for 15 minutes at 60°C (c) one ply of prepreg held for 15 minutes at 80°C
Figure 3.6	SEM images of cross-sectioned AS4/8552 prepreg samples. For condition two, vacuum pressure was applied during heating: (d) one ply of prepreg held for 15 minutes at 40°C (e) one ply of prepreg held for 15 minutes at 60°C (f) one ply of prepreg held for 15 minutes at 80°C
Figure 3.7	Close up SEM of 40°C vacuum used to take dynamic contact angle from regions where resin curved between two fibres
Figure 4.1	DIC test setup
Figure 4.2	Calibration panel (9 x 4 inches)
Figure 4.3	Cycle 1-One hold cycle: Ramp from -5°C To 180°C at a rate of 3°C /min. Hold isothermally at 180°C for 120min. Ramp down to -5°C at 3°C /min. Transition regions are marked on the plot. It is seen that the cure does not progress until the end of the eating ramp, when curing begins it does so rapidly reaching the max cure soon after entering the hold
Figure 4.4	Prepreg sample [0] ₄ layup with speckle pattern applied
Figure 4.5	Resin sample experimental temperature cycle: 10°C/min ramp 180°C hold for 60 minutes, uncontrolled, uncontrolled cool down
Figure 4.6	Cure and viscosity profile for resin sample test
Figure 4.7	DIC principal stain data of the resin in-plane. A significant increase in strain begins after 60°C followed by a larger shrinkage. Little change in strain is seen after this point
Figure 4.8	Resin sample height development over temperature. Initially the sample grows, shrinking slightly before and during the hold
Figure 4.9	Resin sample area change over temperature. There is no apparent expansion in-plane. There is however, a significant shrinkage in the sample as it is heated. Little change in strain is seen after this contraction
Figure 4.1	0 Resin sample during the heating ramp. The majority of strain change occurs during this time. The large change in size occurs between 75°C and 126°C after that point it is difficult to see a significant difference in size
Figure 4.1	1 Temperature driven dimensional changes due to heating. As heat is applied the contact angle between the resin and substrate will increase. The surface tension will draw the resin together while growing to a critical height
Figure 4.1	2 DIC test on 4 ply sample- P13, temperature cycle 1. (a) Strain vs. temperature plot and (b) strain vs. time plot

Figure 4.13 Zone breakdown for initial DIC test done on 4 ply sample-P13, temperature cycle 1. (a) Strain vs temperature plot (b) strain vs time plot
Figure 4.14 Zone 5 of P13, finding the CTE _{Glassy} base on the cool down region. The linear best fit of the strain and temperature plot was used to find the CTE
Figure 4.15 Cure shrinkage response of 4 ply sample P13 during the isothermal hold at 180°C of temperature cycle 1
Figure 4.16 Cure shrinkage coefficients for a 4 ply sample P13 during the isothermal hold at 180°C of temperature cycle 1
Figure 4.17 The pre-gelation coefficient of cure shrinkage varies based on hold temperature- Test P13, cycle 1: 3C/min to 180 hold for 120 min cool at 3C/min. Test P14, cycle 2: 3C/min to 150 hold for 120 min cool at 3C/min. Test P19, cycle 3: 3C/min to 120 hold for 240 min cool at 3C/min. CCS was found by taking the linear fit of the pre- and post-gelation sections of the curve. Post-gelation the rate of cure shrinkage increases
Figure 4.18 Zone 3 for sample P13. Little change in strain is seen after 130°C. Cure starts developing at about 106°C and the rate of curing begins to increase at around 125°C.
Figure 4.19 Shrinkage due to core saturation results in Zone 2 for test P13. The observed stain drop occurs between 35°C to 105°C72
Figure 4.20 Average shrinkage in Zone 2 for 1 and 4 ply samples. There is higher variability in the 1 ply samples compared to 4 ply samples where multiple plies can even out some of the variability of the material
Figure 4.21 Zone 1 for test P13 where Tg < T. The CTE value (taken as the slope between - 3.5°C and 25°C) is 89 ×10-6 °C-1 found by taking a linear fit to this section of the plot
Figure 4.22 Two Hold Cycle: Ramp from -5°C to 100°C at a rate Of 3°C /min. Hold isothermally at 100°C for 30min. Ramp down to -5°C at 3°C /min. Ramp from -5°C to 180°C at a rate of 3°C /min. Hold isothermally at 180°C for 120min. Ramp down to -5°C at 3°C /min. Curing does not develop significantly until the second hold
Figure 4.23 Two Hold Cycle: Ramp from -5°C to 100°C at a rate Of 3°C /min. Hold isothermally at 100°C for 30min. Ramp down to -5°C at 3°C /min. Ramp from -5°C to 150°C at a rate of 3°C /min. Hold isothermally at 150°C for 120min. Ramp down to -5°C at 3°C /min. Curing does not develop significantly until the second hold
Figure 4.24 Two Hold Cycle: Ramp from -5°C to 100°C at a rate of 3°C /min. Hold isothermally at 100°C for 30min. Ramp down to -5°C at 3°C /min. Ramp from -5°C to 120°C at a rate of 3°C /min. Hold isothermally at 120°C for 240min. Ramp down to -5°C at 3°C /min. Curing does not develop significantly until the second hold and do to the low hold temperature there is a gradual increase in cure compared to other temperature cycles
Figure 4.25 P22- Direction 2 linear strain response over the temperature of a 4 ply prepreg sample, saturation test with temperature Cycle 5

Figure 4.39 Schematic representing stress states resin is up under when heated and cooled. When cooling the resin pulls on the fires as a result the resin feels a tensile force. When

Figure 5.1: 3D DIC transverse strain map of the sample 15 minutes into the 60°C isothermal hold. The orientation of the ply is marked, the fibres are in the direction of the Y-axis.

Figure 5.4: SEM image of a section of the AS4/8552 prepreg sample cross-section after the heating cycle. Black spots are priority in the ply...... 112

	sample sandwiched between pre-cycled porynnide min sneets that have been coat	zu
	with 3 layers of Freekot release agent	143
Figure C.7	7 Calculated through-thickness strain response reported by TMA with a 0.01 N	
C	applied probe force.	146

Figure C.8 Calculated throug	h-thickness strain response repo	orted by TMA with a 0.1N applied
probe force		

List of Supplementary Material

Video1 P13 exx 3D Test Video2 P22 exx 3D Test 1st hold zeroed, ramp 1 focus Video3 P22 exx 3D Test 2nd hold zero, full cycle Video4 P22 exx 3D Test 2nd hold zero cooldown,1 ramp focus

List of Symbols

Sign	Description	SI Unit
lo	Initial length	mm
$\Delta 1$	Change in length	
3	Strain	
ε11	In-plane thermal strain, fibre direction	
ε22	In-plane thermal strain, perpendicular to fibre direction	
833	In-plane thermal strain, through thickness of the ply	
ΔT	Change in temperature	
α_1	Linear coefficient of thermal expiation in direction 1, the fibre direction	10 ⁻⁶ °C ⁻¹
α ₂	Linear coefficient of thermal expiation in direction 2, perpendicular to the fibre direction	10 ⁻⁶ °C ⁻¹
α ₃	Linear coefficient of thermal expiation in direction 3, the thickness direction	10 ⁻⁶ °C ⁻¹
ϕ_{f}	Fibre volume fraction	
E_{f1}	Tensile modulus of the fibre in direction 1	GPa
E_{m1}	Tensile modulus of the matrix in direction 1	GPa
$lpha_f$	Linear coefficient of thermal expiation of the fibre	10 ⁻⁶ °C ⁻¹
$lpha_{ m m}$	Linear coefficient of thermal expiation of the matrix 10 [°]	
υ12	Poisson ration	
θf	Poisson ratio of fibre	
υm	Poisson ratio of matrix	
Tg	Glass transition temperature	°C
Q	Fluid flow rate	$m \cdot s^{-1}$
k	Permeability of a porous medium	m^2
μ	Viscosity	Pa S
А	Area	Mm^2
L	Length	mm
ΔP	Pressure gradient	Pa

Pc	Capillary pressure	Ра
γ	Surface tension m.	
R	Radii of curvature	
θ	Contact angel	
$\gamma_{ m so}$	Surface tension between the surface and the air m	
$\gamma_{ m sl}$	Surface tension between the surface and liquid mJ/	
$(\varepsilon L - CS)m$	Linear cure shrinkage response of the matrix	
$(\varepsilon V-CS)m$	Volumetric cure shrinkage response of the matrix	
$(\varepsilon V - CS)m$ -Total	Total matrix cure shrinkage	10 ⁻⁶ °C ⁻¹
χ	Degree of cure	
Vm	Volume fraction of the matrix	
PL	Laplace pressure	Pa
P _H	Hydrostatic pressure	Pa
ρ	Density	
g	Gravity	m/s^2
e	Critical height	mm
ho	Initial thickness of the total system	mm
fp	Thickness of the polyimide film	mm
p_0	Initial prepreg thickness mm	

List of Abbreviations

AFP	Automatic Fibre Placement
CCD	Charge-Coupled Device
CCS	Coefficient of Cure Shrinkage
CFRP	Carbon Fibre Reinforced Polymer
CTE	Coefficient of Thermal Expansion
DIC	Digital Image Correlation
DMA	Dynamic Mechanical Analysis
DOC	Degree of Cure
DSA	Drop-Shape Analysis
PAN	Polyacrylonitrile
PI	Polyimide Film
PP	Prepreg
RTM	Resin Transfer Molding
SEM	Scanning Electron Microscopy
Т	Total Sample Size
Tg	Glass Transition Temperature
TMA	Thermomechanical analysis
UD	Unidirectional
XP	Cross Ply

Acknowledgements

I have been lucky to have had so many people supporting me while completing this thesis. I would like to take this time to thank them all for their contributions.

To start, I would like to thank my supervisor, Professor Anoush Poursartip. The guidance you provided made this thesis possible, and your passion for the field has taught me so much. I look forward to furthering the skills you have taught me as I move forward in my professional life. I would also like to thank Dr. Navid Zobeiry for advising me. I am grateful for your counsel and the dialogues that helped shape this work. Furthermore, I thank you for the many hours we spent musing over the periodic table of elements and discussing the universe.

Additionally, I would like to thank Professor Göran Fernlund and Professor Reza Vaziri for their thoughtful input.

It has been my pleasure to work as part of the Composites Research Network at UBC. I want to thank all the past and present members who have been a part of my studies. In particular, I would like to thank the research associates at CRN, Dr. Christophe Mobuchon, Dr. Casey Keulen and Dr. Navid Zobeiry, for all their help to make this project as success, and for always sharing their chocolate.

Thank you to Suzana Topic, lab manager extraordinaire, for all the guidance and support, as well as the many enjoyable conversations.

To the current and past graduate students, Sahar Abouali, Nasser Arbabi, Nima Bakhshi, Cheng Chen, Hubert Courteau-Godmaire, Dr. Janna Fabris, Shayan Fahimi, Erfan Forghani, Margarita Galper, Dr. Kamyar Gordnian, Shaghayegh Kiafer, Mohammad Mohseni, Scott Nesbitt, Duncan Pawson, John Park, Dr. Andrew Stewart and Gavin Tao, thank you for greeting me each day with a warm welcome. And to all those researchers who visited our group, thank you for sharing your different perspectives. I enjoyed our stimulating conversations. I would especially like to thank the members of my cohort, Duncan Pawson, Hubert Courteau-Godmaire and Cheng Chen who started this journey with me. I am grateful to have such supportive friends and colleagues. And to the amazing women I had the pleasure of working with, Professor Martine Dube, Dr. Janna Fabris, Shaghayegh Kiafer, and Sahar Abouali, I thank you for your community, your validation and your support. You continue to inspire me.

I especially want to thank Dr. Karl Nelson, from the Boeing Company for his guidance that directed me to this program, and his continued support throughout.

I want to thank the friends I have made during my time in Vancouver. Thank you for the joy and support you bring me.

And finally, I would like to thank my family who contently inspire me, and who have always supported my desire to learn. You are my heroes. I would especially like to thank my parents, Anne and Bob Duffner, for their unwavering support during this journey; I know it wasn't easy. Your dedication to my education has been one of the greatest gifts in my life. Thank you.

Dedication

To the educators in my life, the teachers, professors, and mentors who worked tirelessly to pass on the tools to uncover many of the secrets this world has to offer.

> 'Nothing in life is to be feared, it is only to be understood. Now is the time to understand more, so that we may fear less.' -Marie Curie

Chapter 1: Introduction

Carbon fibre reinforced polymer (CFRP) composites have been shown to be beneficial to the advancement of industries that value enhanced properties over material cost. Industries that have turned to composites include aerospace, automotive, energy, and sports [1,2]. The appeal of composites stems from their high strength to weight ratio, the design control of the material stiffness, and the ability to reduce the number of parts (i.e., part consolidation) to reduce the number of joints and increase fabrication rates. Proper application of CFRPs can have significant benefits, but this requires a thorough understanding of the manufacturing process in order to control manufacturing-induced defects that might adversely impact their performance.

Currently, approximately 70% of the composite market is dominated by thermoset-based composites [3]. A thermosetting polymer undergoes several transitions during the curing process, from a viscous fluid to a rubbery viscoelastic solid and eventually a glassy solid [4]. The shift from fluid to a solid state is termed gelation. During gelation a macro 3D network of polymer chains forms, extending to all boundaries. Resin modulus starts to build up, and post-gelation stresses (i.e. residual stresses) are locked in the material, which affects the quality of the end-part.

Composite part processing can be broken into two distinct methods. In the first method, dry fibre is laid down and later infused with a low viscosity resin. An example of this type of processing method is resin transfer moulding (RTM) or infusion. The second method is when a higher viscosity resin is pre-impregnated into the fibre bed forming a material referred to as prepreg. This second process is the main focus of this work. For both infusion and prepreg processes the laws of fluid dynamics that govern the flow of a liquid through a porous media, defined by Darcy's Law are important in describing the material behaviour, however the difference in viscosity between these methods has caused the focus of research in these areas to differ greatly. In infusion, the fast moving liquid flows through a dry fibre bed in-plane and is drawn into the material by a pressure gradient. Many researchers have studied the laminar flow of resin into the dry fibres and developed a strong fundamental understanding of the fluid flow for this case [5–11]. Prepreg studies on the other hand present a more complex initial state that makes applying simple Darcy's Law calculations difficult. During the manufacturing of prepreg the outer surfaces of a ply becomes

highly saturated with resin while the core of the ply stays dry. In most cases this inconsistent resin distribution is ignored and the ply is considered fully saturated. Research that models the flow of gas out of the material in plane dose not consider the saturation of the resin through the thickness of the ply [8,12]. In general, process modelling of composite material can be broken into a few different approaches. Two of the classical approaches consider the system as[13–18],

- A liquid infiltration of an elastic porous media.
- A continuum made of a viscoelastic or hyper-elastic deformable solid with a low modulus pre-gelation.

Given the complexity that exists in the pre-gelation region, in order to optimize process parameters and reduce defects, process simulation tools capable of capturing the evolution of material properties through these transitions are needed. Insight gained from experiments on the behaviour of the system are used to improve the process models.

Traditionally, experimental characterization of prepreg behaviour has focused on the post gelation region of the material. The response of the material in the pre-gelation region is difficult to capture using traditional testing methods, as working in this state is similar to trying to work with a hot marshmallow: any time it is handled it deforms and sticks to things. Despite the challenges in working with this material, it is imperative that this phase be understood as the field shifts to manufacturing techniques that involve handling the pre-gelation material. In recent years, there has been a shift toward implementing fast and automated fabrication methods including automatic fibre placement (AFP) and forming. This trend is well captured by the increase in research activities in the respective areas. For example, since 2015 the cumulative number of papers published on these topics has increased from 368 to 670 according to Web of Science search results¹. These fabrication methods manipulate the raw prepreg material, and without a strong

¹ Web of Science Search Results for search terms "Automated Fiber Placement" and "Composites" between 1900 and 2015: 128 publications. Between 1900 and 2020: 291 publications. Search Results for search terms "Forming" and "Prepreg" between 1900 and 2015: 240 publications. Between 1900 and 2020: 379 publications.

understanding of the mechanisms at play, actions performed on the initial state of the material can influence the overall part quality.

Although most of the literature focuses on the post-gelation behaviour, there are a few studies that have looked at the material before gelation. These studies have noticed the effect of the initial condition on the response of the material that later lead to the development of defects. Recent works have shown clear links between defects such as wrinkling, porosity, and residual stress to the initial state of the material [19–21]. Additionally, the study of prepreg tack, or the measure of the stickiness of a ply, demonstrates the importance of understanding the initial condition of the material. Studies have shown that tack is linked to the formation of wrinkling or puckering of the material during layup [22] and that tack can vary as a function of out-time, and environmental conditions [22–25]. The diversity in research areas (wrinkling, porosity, residual stress, tack, forming, AFP) that have begun to detect the impact of the pre-gelation state on the final part highlights the need for greater understanding and more robust test on this state.

Despite the need, there is still the challenge of finding a method that accurately captures the pregelation phase. An approach to understanding the material behaviour is looking at the free strains in the material. The free strains induced in the material thermally or through curing, lead to dimensional changes. Measuring these strains, therefore, provides information on the underlying material behaviour. However as mentioned before, the "hot marshmallow" like qualities of the material pre-gelation makes it challenging to observe the strain response during processing without influencing the material.

Volumetric dilatometry, thermomechanical analysis (TMA), or dynamic mechanical analysis (DMA), are well-established methods for tracking dimensional changes in the material, however these methods, outlined in Chapter 2, focus on the post-gelation behaviour [26–30]. The work presented in this thesis focuses on understanding the pre-gelation state of the material and how it impacts the processing of thermoset prepregs. New test methods that avoid problems seen in more conventional strain tracking techniques are explored. One technique utilized in this work is Digital Image Correlation (DIC), a non-contact, in-situ, strain measuring technique. By observing changes to a speckle patterned surface, full-field deformation vectors are measured for strain measurement.

The second main technique in this study is Scanning Electron Microscopy (SEM) which was used to observe resin flow in porous prepreg at a microscopic level. The application of these methods allowed for a greater understanding of the effects of the resins fluid state pre-gelation. Results reveal the significant impact capillary flow has on the material behaviour during processing. Current work contributes to extending the understanding of the evolution of free strains postgelation to the pre-gelation regime, specifically related to partially-impregnated prepreg, and the effect of the surface tension-induced capillary flow. The work presented here elucidates some of the unknowns surrounding prepreg behaviour at the start of the processing cycle and can be used to improve process simulation tools.

Chapter 2: Literature Review, Background, and Objectives

2.1 Processing

As introduced in the previous chapter a composite can be made by placing fibres down on a tool and then adding resin, known as infusion. Alternatively, a composite can be made by laying down a material with resin pre-impregnated into fibres referred to as prepreg.

2.1.1 Prepreg Fabrication

Prepreg refers to fibre tape or woven fabrics partially impregnated with resin using a hot melt or solvent dip process [31]. Resin distribution varies for different materials, but most are partly impregnated. Initial resin location and the progression of cure are both key factors that affect the behaviour of the composite as a whole and will be evaluated through this study. For unidirectional composite, a conventional orientation is used when describing parameters in different directions. Figure 2.1 shows the conventional orientation. In the lamina, direction 1 is along the normal axis of the fibres. Direction 2 is in the same plane as direction 1, perpendicular to the fibres. Direction 3 is the through-thickness direction.



Figure 2.1 Schematic of unidirectional ply with a conventional coordinate system, direction 1 is parallel to the fibres, direction 2 is perpendicular to the fibres, and direction 3 is through the thickness of the ply.

The work presented in this thesis focuses on the processing of prepreg material, specifically unidirectional thermosetting prepreg manufactured using a hot melt process. The fabrication of prepreg and characteristics of thermosetting resin systems is discussed in the following sections.

2.1.2 Carbon Fibre Fabrication

The carbon fibres provide the strength and stiffness to the composite. Carbon fibres are commonly made of polyacrylonitrile (PAN), which undergoes high heat treatments to gain high strength properties. Initially, PAN fibres go through a stabilization process called oxidization. During this stage, the fibres are heated in air to temperatures ranging from 200°C to 400°C. After the fibres are stable, they are placed in an inert environment and exposed to temperatures around 1000°C. This second stage is called carbonization. At this time any non-carbon elements are removed. Finally, the fibres go through a graphitization step where they are treated at a higher temperature, around 3000°C. Graphitization rearranges the carbon-carbon bonds increasing the crystalline structure in the fibre. During this step, Young's modulus in the fibre direction is increased [32]. Finally, after fabrication, the surface of the fibres is treated and sizing (an epoxy without curing agent) is applied. This treatment helps increase the adhesion to the polymer matrix as well as protect the fibres as they are being handled and formed into fabrics [33]. Fibres are produced in bundles called tows each containing thousands of fibres [34]. Once tows are formed the resin matrix can be applied.

2.1.3 **Prepreg Fabrication-Hot Melt Procedure**

There are several ways to combine resin and fibres; this work focuses on prepreg material manufactured using a hot melt process. This is a standard prepreg fabrication process in which fibres are impregnated with resin in a melt form or in a resin film, which has a controlled thickness. Heat and pressure are used to combine the resins with the dry fibres. Immediately after resin and fibre are combined, the prepreg material is cooled before being rolled onto a spool [33].

2.1.4 Thermoset Resin

Resin systems used in advanced composites are either thermoset or thermoplastic polymers. This work will focus on thermoset systems. A thermosetting polymer undergoes a chemical change when heated. Cross-linked networks are formed, changing the polymer from a low viscosity fluid to a gelled or rubbery material [33,35]. Curing is not the only parameter that can affect the material response, temperature also has a significant effect. A schematic of a process map showing the relationship between the degree of cure and temperature is shown in

Figure 2.2. Plotted is the glass transition temperature (Tg). When a thermosetting polymer is at a temperature above its Tg it is in a liquid/rubbery state and below in a glassy state. The point of gelation is also indicated. Below the gelation point resin acts like a liquid, or if temperature is below Tg resin acts as an un-gelled glass.



Figure 2.2 Process map indicates the cure and temperature dependence of each state resin goes through. Each state will result in a different material response, so understanding and defining each region becomes important when talking about materials thermal and curing behaviour.

2.1.4.1 Gelation

Gelation is the point when the resin transitions from a viscous liquid to a rubbery state [35]. Flory states that gelation of a polymer, "if due to infinitely large molecules, would occur when fewer than one intern-molecular linkage had been formed per unit of the entire polymer mixture[36]" Gelation for a particular material occurs at a constant degree of cure that is independent of curing temperature [37]. At this point, the resin can no longer flow.

After gelation, the material starts to act more like a solid. There is a transition from viscositydominated behaviour to one defined by the modulus of the resin. As cure progresses past gelation, the modulus is formed and begins to build. Stresses are locked into the material, and resin is said to have memory after this point. Figure 2.3 shows a schematic of the polymer chains forming crosslinks.



Figure 2.3 Schematic of the transition at the gelation point due to crosslink formation. As this chemical reaction occurs viscoelastic liquid resin transitions to a solid. This transition is non-reversible. When links are formed the resin is no longer able to flow freely.

onward.

2.1.4.2 Glass Transition Temperature (Tg)

The glass transition temperature marks the point at which polymer transitions from a glassy solid to a semi-flexible material. The cross-links are still present at this point, but there is increased mobility in the links. This transition marks the temperature limit at which point the structural integrity of the composite is lost, and there is a significant drop in mechanical properties [33,35,37].

2.1.4.3 Vitrification

Vitrification is the temperature point where the resin transitions from a liquid/rubbery state to a glassy state. The point at which this transition occurs is dependent on the cure cycle. It is defined

as the point where the glass transition temperature (Tg) of the material is equal to the cure temperature. When the resin vitrifies, cure stresses develop [33,35,37].

2.1.5 Free Strains Induced During Composite Processing

Free strains are generally broken into three groups, thermal changes, matrix phase changes, and moisture absorption[38]. As a whole, composite parts change shape due to these free strains and in an unbounded body no stress is developed as a result of these strains. For this work the main focused will be on thermal changes and matrix phase changes.

Thermal changes come from increasing or decreasing heat energy in the system causing the composite (resin and fibres) to expand or shrink [39,40]. Matrix phase change due to curing causes a volumetric change in thermosetting resins. As mentioned previously the formations of crosslinks occurs as a thermoset polymer is heated. More crosslinking leads to a decrease in resin volume.

As mentioned these strains, if isolated, do not form stress. However, residual stresses can be a result of mismatching strain from different components in the system. Mismatched strain values between resin and fibres or part and tool are interactions that can lead to the development of residual stresses. Residual stresses can lead to deformation in the part such as part spring-in. Spring-in is described as the effect when a deformation in the final shape is induced into the part to release residual stresses build up during processing. As a result of changing shapes in a composite part, the structural integrity of the product could be at risk. In addition to residual stress, porosity and wrinkling and defects in the parts surface are all common defects in composite parts that are closely tied to the strain induced in the material through processing [21,41–46]

2.1.5.1 Thermal Expansion

Adding heat energy to the system causes a composite part to change its shape. At heightened temperature, atoms vibrate faster, and the space between them expands, leading to an expansion of the material. As heat is removed from the system, the material contracts as the vibrating atoms slow down. The coefficient of thermal expansion (CTE) is the property of a material that captures the thermal behaviour of a material leading to dimensional changes.

In isotropic materials, CTE is defined as the strain, or change in length, in a material relative to the change in temperature. CTE can be found by taking the change in strain divided by the corresponding change in temperature, as seen in Figure 2.4.



Temperature (°C)

Figure 2.4 Graphical representation of the coefficient of thermal expansion (CTE). The thermal expansion of the material can be quantified from change in length and temperature data. The change in length divided by the original length is the strain, so, to simplify the CTE expression the change in strain is divided by the change in temperature.

Since a composite is made from two distinct materials acting together, the thermal behaviour is more complex. Resins and fibres have mismatched expansion values caused by differences in their individual physical and chemical properties. Carbon fibres typically have a very low CTE in the direction of the fibre (direction 1), whereas resin generally has higher CTE values. Furthermore, resin has different CTE values as it cures. Starting as a viscous liquid above Tg, the uncured resin has a high coefficient of thermal expansion. As cure develops, the ability to expand is reduced due to the formation of chain-links. Therefore the CTE of the rubbery and glassy resin is progressively lower. There are three distinct CTE ranges that can be captured depending on the progression of cure and the temperature relative to glass transition temperature (Tg). The first is CTE_{Liquid}, resin

is above Tg and has not cured pass the gelation point (T>Tg and X<Xgel). When the resin is above Tg and cure has progressed passed gelation the thermal expansion is defined by the $CTE_{Rubbery}$ (T>Tg and X>Xgel). When resin temperature is below Tg and un-gelled or gelled the material is considered glassy and therefore the CTE_{Glassy} is used to capture the thermal response (T<Tg and/or X>Xgel).

According to micromechanics, to determine the CTE of the composite, a combination of the fibre and resin CTEs are needed. Additionally, composites are orthotropic materials, and therefore, thermal expansion is directionally dependent.

The following assumptions based on micromechanics have been made without consideration for the state (liquid, rubbery, or glassy) of the material. In general, one can assume the thermal expansion in the direction of the fibres (strain 1) is close to zero as fibres constrain expansion. The other dimensions are not confined by the fibres, and they should be primarily influenced by the thermal expansion of the resin. The assumption can be made that strain in the transverse direction and the through-thickness direction are equivalent (Equation 2.3). Equations 2.1, 2.2, 2.3 are used to calculate different CTEs in the composite [35].

$$\alpha_1 = \left(\frac{\phi_f E_{f1} \alpha_{f1} + (1 - \phi_f) E_{m1} \alpha_{m1}}{\phi_f E_{f1} + (1 - \phi_f) E_{m1}}\right)$$
2.1

$$\alpha_{2} = \phi_{f} \alpha_{f} (1 + \upsilon_{f}) + (1 - \phi_{f}) \alpha_{m} (1 + \upsilon_{m}) - \alpha_{1} \upsilon_{12}$$
2.2

$$\alpha_2 = \alpha_3 \tag{2.3}$$

The CTE is represented as α , subscripts indicate the direction (1, 2 or 3) and fibre or matrix (f or m). The volume fraction of fibre in the composite is represented as ϕ_f . The modulus of the fibre and matrix are E_{f1} and E_{m1} . The composites Poisson's ratio is v_{12} .

2.1.5.2 Cure Development

As mentioned, when a thermoset resin cures, it transitions from a viscous liquid to a glassy solid. This transition occurs as the bonds holding together the epoxy switch from weak Van der Waals bonds to shorter, stronger covalent bonds [33,35,39,40] These bond creations are called crosslinks. As mentioned previously, when discussing thermoset resins, the development of crosslinks leads to the gelation of the viscous resin. In addition to changing the physical state of the resin increased crosslinks leads to a decrease in the overall volume of the resin.

In a composite part, the shrinkage caused by cure, or cure shrinkage, will cause an overall volumetric shrinkage of the part. However just as CTE is directionally dependent the effect of cure shrinkage depends on the orientation of the part. For a ply of UD prepreg the fibres constrict the shrinkage in direction 1 and force the total volumetric shrinkage to be split equally between direction 2 and 3.

Figure 2.5 is adapted from literature to represent the volumetric response of the prepreg to free stresses induced by thermal and curing through a simple heating cycle.


Temperature (°C)

Figure 2.5 Schematic of the expected behaviour of a thermoset polymer composite during processing adapted from literature[47]. Between a and b the resin is in the liquid stage and very low curing if any occurs. It is expected that thermal expansion dominates the materials behaviour during this period. Between b and c the resin is still in the liquid state however some curing has begun and there is a mixed response as the effect of cure shrinkage increases. Between c and d the temperature is held and the effects of cure are isolated. A large decrease in volume occurs. Form d to e the curing is assumed to have stopped and only thermal contraction is seen.

2.2 Fluid Flow Through Porous Media

With infusion processes a low viscosity resin is injected into dry fibres saturating them by an applied pressure gradient. This pressure gradient is created from the inlet, outlet, and capillary pressures [5,9,48–53]. Many researchers have looked into the flow of resin for infusion processes, conversely, few have looked at resin flow progression during prepreg processing. One study looked at the effect of resin flow in prepreg forming at an elevated temperature and saw the effects

of capillary flow. The resin flow due to capillary effects showed resin moving to the core of the prepreg. This was seen to result in a reduction of inter-ply separation during forming compared to forming at lower temperatures. [51]. The following section describes the fundamental laws that govern the behaviour of resin through the fibre bed.

2.3 Surface Tension

Surface tension is the surface energy needed to hold a liquid in shape. It is caused by a force imbalance at the molecular level [56,57]. In the bulk of a liquid, each molecule feels an equal pull by its neighbouring molecule, but the molecules at the edge of the liquid have a stronger pull in the direction of the bulk creating this boundary.

Surface tension of a material can change based on the interface properties defined by Young's Equation.

$$\gamma \cos \theta = \gamma so - \gamma sl \qquad 2.4$$

Where γ is the surface tension of the droplet, γso is the surface tension between the surface and the air and γsl is the surface tension between the surface and the liquid. θ is the contact angle between the surface and the droplet. To find the surface tension, the contact angle can be measured, and Young's equation can be applied.

2.4 Capillary Pressure

The capillary pressure is the hydrostatic pressure differential, which occurs when crossing the interface of two separate fluids. This pressure is a function of the surface tension and the geometry of the interface. It is defined by the Young-Laplace equation [57],

$$\Delta P_c = \gamma (\frac{1}{R_1} + \frac{1}{R_2})$$
 2.5

In this equation R_1 and R_2 are the radii of curvature of the surface. As mentioned, many researchers have examined the effects of capillary pressure on RTM systems, but few evaluated prepreg systems.

2.5 Darcy Flow

Darcy's law comes from the Navier-Strokes equation which describes the flow of liquid through a porous medium caused by a pressure imbalance. The fluid flow rate, Q, found by Darcy's law, is shown in Equation 2.6.

$$Q = \frac{-\kappa A \Delta P}{\mu L}$$
 2.6

In Darcy's Law, κ is the measure of the permeability of the porous medium and the viscosity of the fluid is μ . The geometry is defined by A, the cross-sectional area, and L, the length travelled. ΔP defines the pressure gradient. The driving force leading to the fluid follow is the pressure imbalance. For composite resin transfer moulding (RTM) extensive research, both experimental and modelling, have been done to understand the importance of Darcy's Law on this process [5,9,48–53]. Researchers have seen the resins flow into the fibre tows due to capillary pressures, which add to the total pressure gradient and increase the flow of resin through a dry fibre bed.

2.6 Initial Condition Effects on Defects

Researchers looking at the development of defects in composite parts have begun to notice a connection between the initial condition of the material and the impacts that the initial state has later in the manufacturing process.

2.6.1 Wrinkling

Stewart has characterized the fibre alignment of unidirectional prepreg from a roll of material as received from the manufacturer [21]. This work showed significantly more fibres were aligned out-of-plane than in-plane. Other researchers have examined the relationship of the untouched material and fibre alignment, predicting some correlation with the position on the roll [58]. In work presented by Stewart optical microscopy and measurements of the fibre geometry were used to determine the misalignment of fibres over a large variety of roll sections. Additionally, studies have found that these misalignments are correlated with wrinkle growth in the material [20,21].

2.6.2 Porosity

Porosity, or entrapped gas, is a common defect seen in composite manufacturing. A large body of work has investigated the different causes of porosity and different techniques to eliminate or

reduce these defects. Much of the work done in this area looks at how the resin and entrapped air are transported from different processing techniques [59,60]. Work done on moisture driven porosity reduction focuses on modification of the cure cycle. Results showed that adding a hold step early at relatively low temperature could prevent the formation of moisture driven porosity [19]. With the exploration into causes and preventative techniques, it is clear that, in the area of porosity, understanding the initial condition of the material and how the material behaves when heated will help develop this area of study.

2.6.3 Prepreg Tack

Tack is a term used to describe the ability of prepreg plies to stick together. This parameter is important as the tackiness of the material determines whether the plies will slip during layup and forming. The slippage between plies has been linked to defects such as wrinkling or puckering during layup. Studies have seen that these propertied changes depending on the environmental conditions such as humidity. Results reported by Wohl, Seferis, et al. [22] showed that tack was inversely related to temperature and humidity and correlated to contact time.

Putnam, Saferis, et al. [23] performed tack experiments on prepreg laid up on the Boeing shop floor and found the ideal tackiness by adjusting processing parameters like line speed, temperature, and resin content. It was found that increasing line speed, decreasing temperature, and increasing resin content led to an increase in tack [23].

In an additional study, it was noted that when the temperature is increased resin flows from the surface to the core of the ply, and with lower surface resin, the tackiness decreases [25].

2.7 Measurement Techniques

As both CTE and cure shrinkage are important properties when modelling the processing of composites, a variety of test methods have been developed to characterize materials. Figure 2.6 shows a breakdown of several of the different test methods presented in the literature.



*Although assumed not to influence the sample a small load applied in this technique does have a significant impact on the pre-gelation behaviour of prepreg.

Figure 2.6 Breakdown of different common characterization techniques for measuring dimensional changes in resin and composite material systems.

The most popular techniques are outlined briefly below. Results from studies performed on HEXCEL AS4/8552 and 8552 resin are summarized at the end of this chapter in Table 2.1 and Table 2.2.

2.7.1 Capillary-Type Dilatometers

A common way to look at volumetric resin shrinkage is by water or mercury dilatometry. In dilatometry, the change in the height of a column of fluid is linked to the change of volume of a material that has been placed in the fluid [35]. Issues that arise when using this method are the sticking of resin to the walls of the tube and the sample size [44]. The sample size is a challenge

in dilatometry. A large thermoset sample will undergo an exothermic reaction, emitting heat during the curing process, making it difficult to distinguish between thermal expansion and cure shrinkage. A small sample reduces the accuracy as the change in volume is smaller and more challenging to detect. Oberholzer et al. used a pressure sensor as opposed to other studies that use visual methods to determine the change in the mercury displaced by resin [62]. In this study, there was an increase in accuracy because of the use of sensors. Although dilatometers can give an accurate view of the volume change, the process involves submerging resin, and the effect of moisture on the resin and the absorption of liquid could influence the temperature of the resin.

2.7.2 Gravimetric Method

The gravimetric method measures the change in the buoyancy of a resin in a known fluid at a controlled cure temperature [63]. This method is reliable and keeps the resin in a stress-free state. The resin density is measured independently first before being placed in a fluid bath. Given the density of the suspension liquid, the change of volume of the resin can be tracked.

Li, Potter, Wisnom, and Stringer [64] looked at the relationship between cure shrinkage and degree of cure for several epoxy resin systems (MY750/HY917/DY073). Their results found that for varying cure cycles, the chemical shrinkage is only a function of the degree of cure, and independent of time and temperature.

Khoun and Hubert [61] also performed gravimetric tests on resin and found that there was a linear relationship between volumetric shrinkage and degree of cure, however at the point of gelation this relationship shifted. They saw an increase in rate of cure post gelation.

2.7.3 Dynamic Mechanical Analysis (DMA)

DMA testing has been performed to measure dimensional changes in partially cured prepreg samples. Ersoy and Tugutlu [65,66] performed thermal scans of curing prepreg to develop a cure kinetic model. A partially cured sample of AS4/8552 prepreg is placed on two flat fixed bottom clamps in a DMA compression test. A very light load (0.1N) was applied by the top clamp. The displacement of the top clamp, which is always in contact with the sample, is a measure of the through-thickness change in the sample. Ersoy and Tugutlu [65,66] found that the thermal expansion of the clamps in contact with the sample was significant and had an impact on the test

results. They made sure to correct for the clamp expansion in their test. Their tests found CTE values for the rubbery and glassy resin state at varying temperature cycles for unidirectional (UD) and cross-ply (X-ply) laminates. The UD tests found the glassy CTE varied from 12.5 to 19.47 x $10^{-6\circ}$ C⁻¹ and the rubbery CTE from 84.80 to 101.4 x $10^{-6\circ}$ C⁻¹. The results presented by Ersoy and Tugutlu [65,66] also showed that through-thickness cure shrinkage strains in X-ply laminates were about double the strain in unidirectional laminates because the fibres constrained the samples shrinkage in-plane.

2.7.4 Thermomechanical Analysis (TMA)

In TMA, a small sample is sandwiched between two plates and the variation in thickness is captured as the sample is heated [28]. This technique applies to both partially cured resin and prepreg.

Using a system similar to a TMA which they called a video extensometer, Garstka, Ersoy, Potter, et al. [26] were able to look at a sample placed between two heating plates that were covered with release film. A digital camera was used to observe changes. They found linear cure shrinkage post-gelation, averaging 0.48 % for UD and 0.98% for X-ply samples of AS4/8552. This study shows unusual behaviour occurring during the pre-gelation regime. Initially, the samples showed a drop in the strain as the temperature increased. Different pre-consolidation steps do not appear to eliminate this strain drop. The authors attributed this behaviour to the consolidation of the sample.

Work done by Hong et al. [29] used a TMA to examine the cure shrinkage behaviour of epoxy resin. To reduce the interaction between the sample and the testing stage silicon slides were used to sandwich the sample. A constant cure temperature was used to capture the cure shrinkage. Comparison between the TMA profile and the cure profile found using a differential scanning calorimeter (DSC) test using the same temperature cycle allowed the authors to calculate the relationship between cure shrinkage and degree of cure. They found that the cure shrinkage curve changed after the point of gelation, increasing to a maximum shrinkage of 4%.

2.7.5 Modified Rheology Method

Tests have been performed by modifying a rheometer to measure both changing viscosity and through-thickness variation [61]. Khoun and Hubert [61] used a Rheometer in a similar way to a TMA; recording the gap between two parallel plates over some time. This test was done on resin samples tested at three different isothermal hold temperatures. The test was divided into two stages. For the first stage the resin was a liquid, a controlled gap and a 15 % strain was set with a 1 Hz frequency. This stage allowed the linear viscoelastic region of the epoxy to be captured. At the point when the viscosity increased to 500 Pas, the normal force was continued at 0.1 N, and the maximum torque was set to 500 μ Nm at 30 Hz. The height of the gap was measured at this stage. This technique was able to capture the volumetric shrinkage after gelation.

2.7.6 Fibre Bragg Grating

Fibre optic cables have been used to monitor cure shrinkage, thermal expansion, and modulus development in composite samples by researchers at the University of Tokyo[67,68]. These sensors are placed into a composite laminate capturing the post-gelation strain induced by processing. Due to the placement of the sensor into the laminate only information on the linear behaviour of prepreg material can be captured.

2.7.7 Optical Methods

Unlike the majority of other tests that examine dimensional change, the use of imaging technology to observe and analyze material does not induce stresses into the material, does not require the material to have any cure advancement, and does not expose the material to a liquid. Due to these benefits, a variety of different methods have been tested to perfect the use of imaging.

Tests performed on small samples of resin involve placing a drop of resin on a substrate and measuring the profile of the drop. Different devices have been used to capture the droplets profile, like a charge-coupled device (CCD) camera [69] and digital microscopy in Drop-Shape Analysis (DSA)[70,71]. Most work in this area has been done on UV-cure, and dental resin systems [69,72,73]. Recently however, this technique has been applied to aerospace-grade epoxy systems [70,74]. This test method has worked well for capturing volumetric cure shrinkage of resin and the

liquid CTE. Still, some issues do occur if/when the resin bonds to the substrate it is on. Additionally, these tests have not been used to look at the prepreg system.

2.7.7.1 Digital Image Correlation (DIC)

A non-contact technique applied to composite prepreg systems is Digital Image Correlation or (DIC). DIC has been proven to track strain development in full or partially cured carbon fibre prepreg samples [26,75–77] and with resins [78]. Preliminary studies using DIC on both resin and prepregs were able to gain information about the material post-gelation capturing cure shrinkage and thermal expansion.

Jackson, Heinz, and Wiggins, [78] studied the pre-gelation behaviour of resin. They used carbon black power to crat a speckle pattern that would flow with the liquid resin and were able to capture the resin flow front using this method. In a different study, Garstka et al. were able to track the through-thickness strain in uncured AS4/ 8551 prepreg as it developed during processing [26]. Results showed the expected cure shrinkage and thermal expansion behaviour post-gelation. The average post gelation linear cure shrinkage values were found to be 0.48% for UD and 0.98% for X-ply samples. In contradiction to the expected behaviour pre-gelation, the authors observed a strain drop pre-gelation that they attributed to consolidation of the fibre bed.

2.7.8 CTE and CS Literature Data

A presentation of AS4/8552 prepreg and 8552 resin CTE and CS collected from literature is presented in the following tables. These values were taken using different measurement techniques and cure cycles which could account for the variance in the data. Additionally, this thesis distinguishes the difference between liquid and rubbery CTE as below or above the gelation point is given by a specific DOC. Most literature does not make this distinction, calling all CTE values taken above Tg rubbery. This table uses DOC and Tg data giving in the literature to differentiate the repotted CTE values between the liquid and rubbery states.

To better compare literature a simple conversion from linear prepreg values to total volumetric measurements were made. The following assumptions were used to make this conversion.

• For XP prepreg samples:

- Assuming that fibres constrain expansion and contraction in directions 1 and 2 the in-plane CTE and CS values are assumed to be 0, unless reported. Therefore, total prepreg volumetric CTE and CS are assumed to be in direction 3.To convert to volumetric resin values the volumetric prepreg values are divided by the resin volume fraction. For AS4/8552 the volume fraction is 0.43 [79].
- For UD prepreg samples:
 - Assuming fibres constrain expansion and contraction in directions 1 the CTE for direction 1 is assumed to be 0, unless reported. Additionally, direction 2 is assumed equivalent to direction 3 unless measurements are given. Based on these assumptions the total volumetric CTE can be found by taking direction 2 or 3 CTE values and multiplying by 2. To convert to the volumetric resin values the volumetric prepreg values are divided by the resin volume fraction.
- For resin samples:
 - Equal expansion in all directions is assumed. Therefore linear values are multiplied by 3 to find the total volumetric resin properties.

			Literature Reported Values			Calculated Volumetric Resin Values					
Material	Layup	Direction	CTE liquid	CTE rubber y	CTE glassy	CTE liquid	CTE rubbery	CTE glassy	Measurement Method	Notes	Ref.
			x 10 ⁻⁶ °C ⁻¹								
EPREG		1			0.21			-	TMA	MRCC*, fully cured, after vitrification	
	UD	2			33.3±0. 7				TMA	MRCC*, fully cured, after vitrification	
		3			34.7±1. 8			159	TMA MRCC*, fully cured, a vitrification	MRCC*, fully cured, after vitrification	
	ХР	1			3.1				TMA	MRCC*, fully cured, after vitrification	[28]
		2			3.9				TMA	MRCC*, fully cured, after vitrification	
		3			53.7			141	TMA	MRCC*, fully cured, after vitrification	
	UD	2			32.6 ±1.8			152	Strain gage	MRCC*, fully cured, after vitrification	
52 PR	ХР	3	373			867			Video extensometer	MRCC, pre-gelation(0.31)	[26]
NS4/85	UD	3		84.8	17.99		394	84	DMA	pre-cured with a modified MRCC (120°C Isothermal for	
₹	XP	3		158.1	34.37		368	80	DMA	360min**), test cycle: room temp. to 250°C at 2°C/min	
	UD	3		91.44	18.83		425	88	DMA	pre-cured with a modified MRCC (140°C Isothermal for	
	ХР	3		166.4	38.47		387	89	DMA	240 min **), test cycle: room temp. to 250°C at 2°C/min	[65]
	UD	3		84.26	19.37		392	90	DMA	pre-cured with a modified MRCC (160°C Isothermal for 180 min **), test cycle: room	
	ХР	3		163	29.88		379	69	DMA	temp. to 250°C at 2°C/min	

Table 2.1 Summary of CTE Values Reported in the Literature for AS4/8552 and 8552

			Literature Reported Values			Calculated Volumetric Resin Values					
Material	Layup	Direction	Direction CTE	CTE RUBBER Y GLASSY		CTE CTE LIQUID RUBBERY		CTE glassy	Measurement Method	Notes	Ref.
			x 10 ⁻⁶ °C ⁻¹	x 10 ⁻⁶ °C ⁻¹	x 10 ⁻⁶ °C ⁻¹	x 10 ⁻⁶ °C ⁻¹	x 10 ⁻⁶ °C ⁻¹	x 10 ⁻⁶ °C ⁻¹			
	UD	3		101.4	12.5		472	58	DMA	pre-cured with a modified MRCC (180°C Isothermal for	
	XP	3		155.7	35		362	81	DMA	120 min **), test cycle: room temp. to 250°C at 2°C/min	
	UD	3		97.47	16.73		453	78	DMA	Pre-cured -fully cured, test cycle: room temp. to 250°C at	
	XP	3		147	42.89		342	100	DMA	2°C/min	
	UD	3	261.2 ± 16.9 275.8		52.5 ± 6.2	1215	1279	244	TMA	liquid-DOC under 0.03, / liquid- DOC 0.03 to 0.2 (40°C	
	XP	3	± 16.4 256.9 ± 8.6 282.3 ± 20.4		58.5± 5.6	597	657	136	TMA	to 150°C) and DOC 0.03 to 0.6 (40°C to 180°C) cure cycle dependent, glassy- fully cured	[80]
	UD	3	± 20.4	74.0 ±3.6	32.3± 2.1		344	150	TMA	Measurement points through	
	XP	3		135.6 ±12.7	52.0± 1.8		315	121	TMA	temperature cycle ***:Rubbery- 230°C, Glassy-	
NI	resin	linear		73.8±7 .4	23.0±9		221	69	TMA	100°C	[80]
8552 RES	resin	volumetric		780	120		780	120	DSA	rubbery CTEs from 0.0 to 0.4 DOC, galssy from ~0.45 to 1 DOC, Estimated Vol.	[70,71]
Average						899.8	373.5	111.0			
Standard Deviation					262.0	60.9	43.8				

			Literature Reported Values			Calculated Volumetric Resin Values					
Material	Layup	Direction	CTE liquid	CTE rubber y	CTE glassy	CTE liquid	CTE rubbery	CTE glassy	Measurement Method	Notes	Ref.
			x 10 ⁻⁶ °C ⁻¹								
						Other I	Liquid Mat	erials			
Honey		volumetric	457– 481			457– 481				Taken at 20°C	[01]
Glucose Syrup		volumetric	389- 395			389- 395				Taken at 20°C	[81]
CYCO M 5320- 1	resin	linear		84.6	46.6		254	140	DIC	Pre-cured to 0.66	[82]
MY750	resin	linear		210	71		630	213	TMA	Cured for 4 hours at 150 °C	[64]
Average Standard Deviation					430.5 39.5	441.9 188.1	176.4 36.6				

* manufacturer's recommended cure cycle (MRCC): ramp of 2 °C /min up to 120 °C and a first hold at 120 °C for 60 min, a second ramp of 2 °C /min up to 180 °C and a second hold at 180 °C for 120 min.

**Temperature Cycle: Heated from 30 °C to 250 C at 3 °C /m – Cooled from 250 °C to 30 °C at 3 °C /m -Heated from 30°C to 150 °C at 3 °C /m – Cooled from 150 °C to 30 C at 3 °C /m – Heated from 30 °C to 150 °C at 2 °C /m – Cooled from 150 °C to 30 °C at 2 °C /m.

Material	Layup	Direction	Reported CS (%)	Calculated Resin Volumetric CS (%)	Measurement Method	Notes	Ref.
AS4/8552	XP	Volumetric	4.9	11	Video extensometer (same principle as TMA)	MRCC*	[26]
PREPREG	UD	Linear	3.0	14	DMA	Calculated from reported data	[66]
	XP	Linear	4.3	10	DMA	Calculated from reported data	[00]
8552 RESIN	Resin	Volumetric	9.6	9.6	DSA	Varying temperature cycles	[70,71]
	Resin	Volumetric	9.8	9.8	NCAMP data	Implemented in Raven modelling software	[83,84]
	I	Average		11.0			
	Standa	ard Deviation		1.6			
				Other Liquid Mat	erials		
CYCOM 5320-1	Resin	Linear	2.57	8	DIC	Pre-cured to 0.66	[82]
MY750	Resin	Volumetric	6.9	6.9	Gravimetric	Cured for 4 hours at 150 °C	[64]
	I	Average		7.3			
	Standa	ard Deviation		0.4			

Table 2.2 Summary of cure shrinkage (CS) values reported in the literature for AS4/8552 and 8552

* Manufacturer's recommended cure cycle (MRCC): ramp of 2 °C /min up to 120 °c and a first hold at 120 °C for 60 min, a second ramp of 2 °C/min up to 180 °C and a second hold at 180 °C for 120 min.

For AS4/8552 there are very few CTE values taken pre-gelation and due to the verity of test methods used the literature reposts a wide range of reported values. Due to the inconstancy in test methods this work will use a range CTE values to compare results. The calculated resins volumetric CTE_{Liquid} values reported in literature range from 780 x $10^{-6\circ}C^{-1}$ to $1279 \times 10^{-6\circ}C^{-1}$. The calculated resins volumetric $CTE_{Rubbery}$ values reported in the literature range from $221.4 \times 10^{-6\circ}C^{-1}$ to $471.63 \times 10^{-6\circ}C^{-1}$. The calculated resin volumetric CTE_{Glassy} ranges from $69 \times 10^{-6\circ}C^{-1}$ to $244 \times 10^{-6\circ}C^{-1}$, a significantly smaller range. The cure shrinkage values calculated for resin range from 6.9% to 14% by volume.

2.8 Research Objectives and Scope

2.8.1 Synthesis of Literature

A survey of the literature shows that there are a variety of areas of research looking at different defects and how the initial condition of the material can be influential in the creation or reduction of these effects. These works have made it clear there is motivation to understand the material on a fundamental level during the pre-gelation state.

The next challenge is determining a way to capture pre-gelation behaviour. Literature shows a wide variety of measurement techniques that are used to characterize the thermal and chemical dimensional changes in a material. Most of the current methods are not non-contact and have a difficult time examining uncured samples. Due to the limitations in current measurement techniques the development of a testing method that does not influence the material through a processing cycle would be beneficial in observing the true pre-gelation behaviour.

2.8.2 **Research Objectives and Scope**

This work is the presentation of data to probe areas in the processing of this material that has previously been underdeveloped. The purpose of this work is to investigate the pre-gelation behaviour of composite prepreg and characterize the free strains which include thermal expansion and chemical shrinkage that occur during processing through the application of not contact measuring techniques. Several objectives have been defined to help focus and guide this research. The objectives are as follows:

- Develop a method to observe the changes in the morphology of a prepreg system at different stages of the heating process, focusing on the fibre and resin interaction.
- Develop a non-contact strain measurement technique that can be used to characterize the thermal expansion and cure shrinkage of composite prepreg material system before gelation.
- Explore the relationship between local variations in dimensional changes observed through non-contact techniques and the internal structure of a ply of composite prepreg material system.
- Characterize the surface of an uncured composite prepreg material system.

Through tackling the objectives laid out here this work hopes to answer the overall question: can the traditional way of thinking about pre-gelation be used in the future or is there a fundamental difference between pre and post gelation that must be accounted for?

2.8.3 Thesis Organization

To accomplish the objectives presented above, this work has broken down the study of behaviour. The flow chart presented here shows the breakdown of this problem. Starting with the microscopic response the fundamental structure of the prepreg is uncovered making the behaviour observed in the macrostructure easier to understand.



Figure 2.7 Flow chart representation of the breakdown of this thesis. Two major paths to evaluate the pregelation behaviour of prepreg are taken, microstructure focused and macrostructure focus. Each discovery made helps uncover the cause of the observed CTE and CS behaviour.

This body of work is organized into the following sections:

Chapter 3: Microstructural Response- This section takes a close look at the interaction between the resin and the fibres in the core of the ply. Scanning electron microscopy is used to characterize the flow of resin into the core. This close look at the microscopic level informs the mechanisms driving the macro-level response discussed in the next chapter.

Chapter 4: Macrostructural Response- This section looks at the macroscopic scale. It is focused on the CTE and cure shrinkage properties of both resin and prepreg. A non-contact technique is used to capture pre-gelation behaviour. The average behaviour of resin and prepreg is examined and for prepreg the local variants in strain are studied. *Chapter 5: Variably in the Structure of a Ply* - Non-contact techniques are used to look at the surface of a ply focusing on the variability of the material. Additionally connections between the micro-level morphology and the macroscopic level behaviour are discussed.

Chapter 6: Summary and Conclusions- This section summarizes the thesis and presents the conclusions of this work. Ways in which this work could be extended in the future based on the outcome of this work are presented.

Chapter 3: The Microstructural Response

3.1 Introduction

AS4/8552 prepreg is manufactured with a hot-melt process, where the resin is impregnated into the dry carbon fibres. In general the surface of the ply will be highly saturated with resin leaving a dry fibre core. Understanding the inconsistency in resin distribution through a ply is essential when trying to understand resin-fibre interaction. Using a scanning electron microscope (SEM), this study was designed to characterize the microstructure of AS4/8552 prepreg. By examining the prepreg microstructure, the interactions between fibre and resin can be explained and built upon later when focused on a larger scale.

3.2 Method

Imaging a single ply of prepreg at the microscopic scale qualitatively expresses the flow of resin through the cross-section of a ply. Holding a ply at different temperatures allowing the resin viscosity to drop, represents different steps on the heating ramp of a basic one-hold cure cycle. In this study, two experimental conditions were tested at different viscosities, and both were compared to a control case. The experimental conditions looked at the effect an applied pressure had on the flow of resin at different viscosities. The first condition had no applied pressure, and the second condition had vacuum pressure applied. A room temperature cross-section was also prepared and imaged as the control.

3.2.1 Material

For this study, the material studied was an autoclave thermoset system, Hexcel AS4/8552 unidirectional (UD) prepreg (HexPly AS4 12K/8552; 35%; 190AW) [85]. The manufacturer's data sheet states that AS4 fibres are made from carbon with a diameter of 7.1µm and a density of 1.79 gcm⁻³ [86]. The resin system is an amine cured and toughened system with a density of 1.30 gcm⁻³. For the particular role of material used in this study, seen in Figure 3.1, the area weight was given as 190 gm⁻² and contained 35% resin by weight. The fibre volume fraction, ϕ_f , is given as 57.42%. Process models for the materials cure kinetics and viscosity development have been previously characterized, developed[83] and implemented in RAVEN simulation software[84]. This study has utilized the material characterization models and exercised though Raven

simulation software to obtain the degree of cure, resin viscosity profile, and gelation point for different curing cycles.

HEXCEL		P. or below
AS4 12K/8552;35%;190AW;	60"	CALIA
000-2012000037	U1IUN-13	Section of the sectio
LOT NO. MFG O P13193-6 229	TY FT	Hexcel makes no warranty, expressed or implied, concerning this
LOT NO. P13193-6 229 SPECIFICATION NO. GMS 4020 1I TY:35 CL:1 GR:190	FT NO. CUST QTY	Hexcel makes no warranty, expressed or implied, concerning this product or its use. See additional labeling and MSDS for precautions.

Figure 3.1 HexPly AS4 12K/8552 roll used in this work. Production details (date, batch, production location, etc.) are specified along with information on the fibre and resin (areal weight, tow bundles details, and resin-fibre volume fraction).

3.2.2 Pressure Conditions

3.2.2.1 Without External Pressure

In the first condition, one ply of prepreg was heated without the application of external pressure. This pressure condition is similar to the environment used for later DIC experiments detailed in Chapter 4. In this case, the resin will flow due to a drop in viscosity caused by heating the material.

3.2.2.2 With External Pressure (1 atm)

In the condition where external pressure was applied to a ply of prepreg, a caul plate (50 mm \times 50 mm \times 10 mm aluminum) was placed over the sample and vacuum bagged to ensure even pressure

distribution. The pressure and temperature will cause the resin to infiltrate the fibre bed under this condition.



Figure 3.2 Schematic of SEM conditions experiment. Two cases are shown, the first prepreg sits on a tool, the second vacuum bagging is added, and the vacuum is applied.

3.2.3 Sample Preparation and Test Set-Up

To examine the effect that different viscosities have on the resin's ability to flow through the fibre bed, each pressure condition was tested at three different temperatures. Cure kinetic models implemented in RAVEN software [83,84] were used to select temperatures that correlate with different resin viscosities. The temperatures selected were 40°C, 60°C, and 80°C, corresponding to viscosities are presented in Table 3.1. Holding for long periods of time at these temperatures will not advance the cure significantly.

TEMPERATURE [°C]	VISCOSITY [Pa.S]
20	29486
40	3454
60	527
80	102

 Table 3.1 Temperatures and Viscosities for Saturation Tests

In this test, one-ply samples of AS4/8552 prepreg were cut into 50 mm \times 50 mm \times 0.2 mm squares. For the first condition, samples were placed on a 4mm thick aluminum tool coated with three layers of Frekote 700-NC release agent. Gently, using a roller, samples were evenly pressed down to ensure contact with the tool. The tool and sample were then moved to the preheated HEATCON heating blanket set to the specified temperature and left to heat isothermally for 15 minutes. After 15 minutes, samples were quenched in a freezer at -25°C, rapidly increasing resin viscosity and vitrifying the prepreg, thus halting resin flow. In the second condition, in which external pressure was applied, samples were placed on the same 4 mm aluminum tool coated with three layers of Frekote 700-NC release agent, a caul plate was placed on top of the sample and was vacuum bagged using a Strech-VAC 2000 nylon sheet. The sample was placed under vacuum pressure for 10 minutes before moving to the heating blanket and followed the same heating and cooling procedures as condition one. Six samples were tested, one for each temperature and pressure condition.

After samples were quenched, they were removed from the freezer. As samples were very brittle due to the low temperature, they were left out until they reach room temperature before being removed from the tool to prevent fracture. Once the sample had been removed from the tool, it could be prepared for the SEM. To avoid any edge effects, analysis was performed on cross-sections taken from the center of each sample.

Due to the soft, malleable state of uncured prepreg at room temperature, it was difficult to get a clean cut for imaging. Several different cutting techniques were tested before selecting the best method for a clean cut. The different cutting tools tried were scissors, rolling blade, large exact-o knife, and small exact-o knife blade. Cuts were examined using SEM and found that the cleanest cut came from the small exact-o knife. The small exact-o knife blade was held at a 60° angle to get the cleanest cut and avoid pulling the fibres. After cuts were made, there was still some debris left on the cross-sections. Scotch tape was used to clean up the edges for better quality images. A piece of tape was pressed to the cross-section, gently patted to ensure even contact with the prepreg ply and then removed. Examination under an optical microscope showed the presence of particulates on the tape after the edge was cleaned. After determining the best cutting method, all samples were cut in the same way. The cross-sections were left to de-gas overnight in a vacuum chamber at room temperature to eliminate any off-gassing that could occur when placed in the SEM. Although there is a possibility of some resin movement overnight the resin flow index does not significantly increase at this temperature (see resin viscosity at 20°C in Table 3.1). The samples were mounted using carbon tape on a small aluminum brick so the cross section would be exposed to the beam. To prepare samples for imaging, an Edwards S150A Sputter Coater was used to coat each sample with gold. Sputtering the sample with a highly conductive material is essential in

taking SEM images, as the composite itself has relatively low conductivity. An FEI Quanta 650 scanning electron microscope was used to examine the prepared cross-sections. An acceleration voltage of 15kV was used to take the images.

3.3 Results and Discussion

An SEM image of uncured AS4/8552 prepreg is seen in Figure 3.3. This sample is the control specimen. Initial observations show inconsistencies in the prepreg morphology. Some areas of the prepreg appear to have been saturated with resin, leaving little to no void spaces, where other areas show a distinct gap in the middle of the fibre bed with high resin concentration appearing at the surfaces of the prepreg ply.



Figure 3.3 One-ply of AS4/8552 prepreg at room temperature. Comparison of regions of high resin content (a) and dry fibre bed area (b). In (a) the prepreg appears to be fully saturated with resin. In Contrast (B) shows a section of the ply where resin has only saturated the top and bottom leaving dry fibres in and a large void in the center of the ply. These inconsistencies in resin saturation are seen through the prepreg.

The inconsistencies seen in the initial condition of the material are important to note as one considers the effect temperature has on resin movement through the sample. For this test, the area of interest was the drier areas. The objective was to see how the resin flow front moves when the prepreg is held at different temperatures. Figure 3.4 shows the control sample for comparison, this sample was not heated and no pressure was applied to the sample. Figure 3.5 and Figure 3.6

visually displays the progressive saturation of the dry core areas of AS4/8552 prepreg as it is being processed.



Control Condition

Figure 3.4 SEM images of cross-sectioned AS4/8552 prepreg samples. The controlled case. No elevated temperate or vacuum pressure was applied.



Figure 3.5 SEM images of cross-sectioned AS4/8552 prepreg samples. For condition one, no pressure was applied during heating: (a) one ply of prepreg held for 15 minutes at 40°C (b) one ply of prepreg held for 15 minutes at 60°C (c) one ply of prepreg held for 15 minutes at 80°C.





Figure 3.6 SEM images of cross-sectioned AS4/8552 prepreg samples. For condition two, vacuum pressure was applied during heating: (d) one ply of prepreg held for 15 minutes at 40°C (e) one ply of prepreg held for 15 minutes at 60°C (f) one ply of prepreg held for 15 minutes at 80°C.

Results from condition one, in which no external pressure was applied, are presented in Figure 3.6 a-c. This condition showed as samples are heated, the thickness reduces. ImageJ [87] image analysis was used to find the average thickness of the plys. From the samples heated at 40°C to the sample heated at 80°C, the thickness changes from 211 μ m to 173 μ m. The same thickness reduction was seen in the samples with applied vacuum pressure (Figure 3.6 d-f) showing a reduction in average thickness from 213 μ m to 185 μ m. Both conditions showed the thickness of an uncured ply approaching the cured ply thickness,180 μ m — the cured ply thickness was found by implementing material properties reported in the datasheet into Equation 3.1[79].

$$CPT = \frac{w_f}{\rho_f \times 10 \times \phi_f}$$
 3.1

The reduction seen in these experiments is not due to curing, as the temperature does not increase enough to progress cure, but is due to resin filling the void spaces and reducing the inconstancies in the ply. A comparison between the expected cured ply thickness and the ply thickness for each case is seen in Table 3.2. For most of the tests the ply thickness is larger than that of the expected cured ply, but the difference becomes less as the testing temperature increases.

	RT	40°C	60°C	80°C
No Vacuum	114%	117%	114%	96%
Vacuum		118%	112%	102%

Table 3.2 Ply Thickness Comparisons-Percentage of Approximate Cure Ply Thickness

Little difference in sample thickness or saturation of the dry core area is seen between pressure conditions for a given temperature, hinting that external pressure is not the driving force for this consolidation. To understand the force driving the saturation it is important to reflect on how fluid moves through a porous media (See Section 2.2). Darcy's law dictates how resin will flow through the fibre bed. As the resin viscosity drops to a point where it can flow there needs to be a pressure differential to drive resin into the fibre bed. For the no vacuum case, capillary pressure, caused by the surface tension between resin and fibre, is the only force in the system that could drive the resin saturation. For case two capillary pressure and the 1atm of pressure applied by pulling a vacuum could lead to saturation. Because there was no significant difference in resin saturation

between case one and case two the capillary pressure must be the driving pressure. The capillary action produced by surface tension is strong enough to draw the resin into the fibre bed and due to the compliable nature of the fibre bed when the resin pulls inwards the fibre bed will deform with it. This deformation can be seen as a consolidation of the material. The capillary effect is caused by the geometry of the system leading to surface tension. Surface tension depends on temperature, so, as the temperature increases, the surface tension force decreases, but so does the viscosity of the resin allowing flow to occur faster. This is seen when comparing the progression of the flow front for samples held at 40°C for 15 min to those held at 80°C for 15 minutes.

These observations about surface tension, capillary flow, and the driving pressures in prepreg led to the discovery of a novel method of measuring the pressure inside the core of the prepreg by Dr. Zobeiry. In a paper presented by Zobeiry [55], the samples presented above were used to determine the dynamic contact angle between the resin and fibres. Figure 3.7 shows a higher magnification SEM image of the 40 °C sample under vacuum pressure.



Figure 3.7 Close up SEM of 40°C vacuum used to take dynamic contact angle from regions where resin

curved between two fibres

Zobeiry [55] used the dynamic contact angles to calculate the capillary pressure inside the core of the material. He developed the following explanation to measure the negative pressure at the symmetry point of resin interface between two fibres for the flow front of resin and cases where the resin is bridging between two fibres.

$$\begin{cases} u_z \neq 0, u_x = u_y = 0 \rightarrow p = -\frac{\sigma}{R} + \frac{\sigma(\cos(\alpha + \theta_d) - \cos(\alpha + \theta_s))}{\frac{e}{2} + d\sin\left(\frac{\alpha}{2}\right)^2}, \theta_d \neq \theta_s \\ u_z \neq 0, u_x = u_y = 0 \rightarrow p = -\frac{\sigma}{R}, \theta_d = \theta_s \end{cases}$$
3.2

In these equations, u is the velocity vector at the interface. The pressure is given as p. σ is the liquid surface tension. R is the radius of curvature measured from SEM images. α is the angle used to mark the triple line of contact between the vacuum-resin-fibre. θ_s and θ_d are the static and dynamic contact angles respectfully.

Using the equations he developed, the capillary pressure in the core was found. Zobeiry reported negative pressures ranging from -10kPa to -50kPa, and in some places, as large as -250kPa. In addition to the purely scientific relevance of Zobeiry's work, the observation of negative pressure can be used to better understand the ways to control defects such as porosity, phase separation, and waviness/wrinkling. This discovery could not have been possible without the techniques developed for this work which captured the microstructure of prepreg at varying points in the temperature cycle. Additionally, the findings Zobeiry presents help to explain the consolidation seen in the test presented in this thesis. Given that the pressure inside the core is negative, and resin flow is driven by the presence of a pressure gradient it is logical that the resin would be drawn into the low-pressure areas leading to the saturation of the core.

3.4 Summary

Focusing on a single-ply at the microscale sets up the fundamental interactions that are needed to understand the larger scale behaviour of prepreg before gelation. Initial observations showed height variability in the morphology of a raw ply of AS4/8551 prepreg. SEM image analysis

showed regions with height resin content and with dry voids within the fibre bed. Although the inconsistencies in the material are not surprising the significant impact these inconsistencies have on the ply is.

This study focused on the regions of a ply that were initially void of resin. It was shown that capillary pressure drives resin to the void regions when the ply is heated. The void spaces, given the resin has enough flow time (low viscosity for a long enough time), will saturate without any external pressure. This study found that holding a ply at 80°C for 15 min was long enough for near complete saturation. As the voids saturated the ply consolidated, showing how the resin flow on a microscopic level can be seen on the macroscopic scale.

The experimental work presented in this chapter also led to Zobery's[55] discovery of negative pressure within the core of prepreg. This discovery supports the self consolidation effects observed in this work.

Chapter 4: The Macrostructural Response

4.1 Introduction

Previous studies cited in the literature using more conventional methods to track strain development in prepreg material hint at the complexity of behaviour seen in the pre-gelation region. As discussed in Chapter 2, previous methods were typically designed to examine strain development in a solid state, and are not ideal for looking at the pre-gelation region. This is because those measuring techniques apply a load and/or involve being in contact with the sample thus influencing the response. In this work, a non-contact technique is developed to observe the in-plain strain behaviour of prepreg material.

Chapter 3 began to explore the pre-gelation behaviour of prepreg by focusing on the microstructure. Close examination of the fibre and resin interface revealed inconsistencies in the ply morphology. Tests showed that in areas starting with height porosity, the surface tension induced capillary pressure draws resin into the core of the material, filling the voids and alters (or modifies) the thickness of the ply in that area.

In this chapter, the in-plane behaviour is explored on a macroscopic level. DIC is used to track strain development in neat resin and prepreg. The DIC measurements give a global measure, as well as local variations in strain.

4.2 DIC Method

Unlike many other characterization techniques, DIC measurements are optical, noncontact, and do not interfere with the material. There are no probes needed for this type of measurement, so the only interface that could constrict movement is between the tool and the part. This method allows us to capture the pre-gelation behaviour of UD prepreg and identify the dominating forces acting on the material. DIC provides an opportunity to view the development of in-plane thermal strains (ϵ_{11} and ϵ_{22}) of a part on a tool. ϵ_{33} is captured, but the strain is not large enough to be distinguished from the noise of the system in these tests. In these studies, we characterized resin and UD prepreg. The sample preparation of each material and heating equipment was different for both resin and prepreg tests. Nonetheless, the basic procedure and DIC equipment set up was the same. Discussion of equipment set up follows.

4.2.1 Material

As with the previous study on the micro-response of composite material, this study continues to focus on Hexcel AS4/8552 UD prepreg material (HexPly AS4 12K/8552;35%;190AW) [79]. In addition to examining the behaviour of this prepreg system, 8552 neat resin is also studied. Both prepreg and resin have been characterized previously, creating cure kinetics and viscosity models that are implemented in RAVEN simulation software [83,84] and used in this study.

4.2.2 DIC Equipment and Calibration

The VIC-3D system by Correlated Solution was used for this study. The DIC set up consists of two digital cameras supported by a rig positioned approximately 100 cm above the sample. The cameras are at a 30° angle toward the sample. Cameras are connected to a computer running VIC-3D image acquisition software. The cameras are focused on the sample, ensuring both cameras have a clear picture. The image should be centred on the sample and look similar for both camera views. Light exposure is also crucial in taking clear images. The sample is illuminated by two LED lamps placed on either side. Fine-tune adjustment of the camera's exposure can be performed in the image acquisition software. The image of the sample should have high contrast without being overexposed. Figure 4.1 shows the DIC equipment set up.



Figure 4.1 DIC test setup

Once the sample is in focus, the system can be calibrated capturing the orientation of the cameras in relation to the sample. For the calibration, the sample is replaced with a calibration panel as seen in Figure 4.2. The calibration panel has target spots on it that are tracked by the Correlated Solutions software to establish the height and angle of the cameras with the stand where the sample will be.



Figure 4.2 Calibration panel (9 x 4 inches)

Several images (typically 10-20) of the panel were taken. Each image shows the panel at a different orientation by varying the calibration panel's angle and location. The Correlated Solutions software can determine the position (height and angle) of the cameras from the calibration images. Once the calibration is complete, the sample can be placed on the heating stage, and the test can begin.

4.2.3 Heating System

Initial tests were conducted using a Heatcon heating blanket to control the temperature of the sample. A 4 mm aluminum tool was placed on the heating blanket. This heating system has primarily been used to study resin behaviour. There were a variety of different substrate treatments tested to try and reduced tool part interaction. Three, four, and six layers of Frekote release agent, as well as a different release agent (Chemleas), were tested. Minimal difference was seen between the release agents and applications. Therefore, the manufacturers' recommendation of three coats of Frekote was used. Through the initial test, the Heatcon system controller's inability to control the cooling rate was identified. This limited the temperature cycles that could be studied.

Resin tests were all performed on a Heatcon heating system. Due to limitations in the system, an alternate system was used for prepreg tests. An Anton Paar Rheometer Peltier heating system that has a temperature range of -20°C to 200°C with fast and accurate temperature control was selected for the prepreg tests. The Peltier substrate is made with a highly conductive coating [88]. To reduce tool-part interaction, the substrate was covered with a non-stick Teflon tape. The Peltier stage has a diameter of 60mm. The size of the stage dictated the sample size allowed for these tests. Although it would have been ideal to look at larger samples or to vary the size and shape of the samples the control in even heating became a limiting factor.

Temperature cycles can be programmed into the Anton Paar Rheometer software. Measurements are collected once per second. The different temperature cycles examined during this study are presented in Table 4.1.

CYCLE NUMBER	HOLD STEPS	STARTING TEMPERATURE	HEATING RAMP	HOLD TEMP/ TIME	COOLING RAMP
0	1/1	20°C	5°C/min	180°C/120min	5°C/min
1	1/1	-5°C	3°C/min	180°C/120min	3°C/min
2	1/1	-5°C	3°C/min	150°C/120min	3°C/min
3	1/1	-5°C	3°C/min	120°C/240min	3°C/min
5	1/2	-5°C	3°C/min	100°C/30min	3°C/min
5	2/2	-5°C	3°C/min	180°C/30min	3°C/min
6	1/2	-5°C	3°C/min	100°C/30min	3°C/min
0	2/2	-5°C	3°C/min	150°C/30min	3°C/min
7	1/2	-5°C	3°C/min	100°C/30min	3°C/min
1	2/2	-5°C	3°C/min	120°C/240min	3°C/min

Table 4.1 Temperature Cycles for DIC Tests Designed To Gel on the Hold

The primary heating cycle used for this study was cycle 1, seen in Figure 4.3. This cycle was chosen because it was a simple one hold cycle and most of the curing developed during the isothermal hold.



Figure 4.3 Cycle 1-One hold cycle: Ramp from -5°C To 180°C at a rate of 3°C /min. Hold isothermally at 180°C for 120min. Ramp down to -5°C at 3°C /min. Transition regions are marked on the plot. It is seen that the cure does not progress until the end of the eating ramp, when curing begins it does so rapidly reaching the max cure soon after entering the hold.

4.2.4 Sample Preparation

Resin and prepreg samples require different preparation methods. The following sections describe both methods.

4.2.4.1 Resin Sample

The behaviour of resin alone is studied before moving to the more complex system of resin and fibres seen in a ply of prepreg. Resin samples were made to examine the in-plane strain behaviour of 8552 neat resin primarily focused on the pre-gelation region. The sample was prepared by peeling the neat resin film off the backing paper and rolled into a small ball. After forming the ball, it was flattened into a small disk. A thermocouple was used to monitor the temperature of the resin.
The resin sample was first heated to 80°C at a rate of 5°C /min. At this temperature, the resin's viscosity is low enough to allow for flow, but does not lead to significant curing if held at this temperature. The disk of resin was placed on the hot tool for five minutes allowing the resin to soften. Small metal shims of approximately 0.3mm thickness were placed around the edge of the tool, and an aluminum plate with a layer of FEP was placed on top of the resin. A brick was placed on top of the plate, gently applying pressure to ensure the top plate made contact with the metal shims. The resin disk spread evenly under the plate and brick. The result was a thin disk with a thickness of approximately 0.3mm. The top plate was left on the sample for five minutes allowing any stresses induced in the material to relax. Afterword the two plates were moved to the freezer, quickly cooling the sample.

After forming and relaxing the sample, the aluminum plate was removed. A speckle pattern was applied to the prepared resin sample using a permanent ink marker. More details on speckle pattern selection are discussed later in this work.

4.2.4.2 Prepreg Sample

Samples of varying thickness were made using AS4/8552 prepreg. Sheets of prepreg were cut into approximately 25mm by 25mm squares. Then samples were made using a unidirectional lay-up sequence of either $[0]_4$ or $[0]_1$. After laying up, samples were de-bulked at room temperature for ten minutes. Once de-bulked, a speckle pattern was applied to the sample (see Speckle Patterns section for more details). Figure 4.4 shows a prepared 4 ply sample.



Figure 4.4 Prepreg sample [0]₄ layup with speckle pattern applied

4.2.4.3 Speckle Patterns

The DIC technique requires a non-repetitive, isotropic and high contrast pattern to track displacements. The software tracks movement by focusing on a small subset of the image and comparing the speckles in that subset with the next image. If speckles are too large, they will take up to much of the subset and make it difficult to see changes, if they are too small the contrast may be reduced making it challenging to distinguish a speckle from the background. Ideal speckles should be at least 3-4 pixels or visible as distinct features. Several different techniques were tried to get the typical speckle pattern for the samples. Table 4.2 compares the techniques and outcomes.

	Aluminum oxide (white powder on back	White powder changed colour to amber as	
Prepreg	prepreg)	resin saturated the Al ₂ O ₂ particles	
	Corn starch (white powder on back	Dissolved into the surface when heated	
	prepreg)		
	Silver permanent ink	Labor intensive, difficult to get size	
	Silver permanent lik	correct	
	Spray paint (white paint with black	High contrast, easy application, lower	
	speckle)	temperature paints did burn	
	Silver permanent ink	Labor intensive, difficult to get size	
Resin	Sirver permanent nik	correct	
	Spray paint (white paint with black	Low contrast, easy application, lower	
	speckle)	temperature paints did burn	

 Table 4.2 Comparison of Speckle Techniques Used To Determine the Best Method to Be Used In DIC Testing

 SPECKLE TECHNIQUE

 OUTCOME

The speckle technique selected for prepreg samples was spray paint. A high-temperature Rust-Oleum white [89] and KRYLON black [90] paint with a matt finish were chosen to withstand the range of temperatures for this test and to reduce any glare on the sample. A thin, even layer of white paint was applied to the surface of the prepreg samples. After the white paint had dried the back paint was used to create a high contrast speckle pattern. The black paint was held away from the sample, pointed at an angle above the sample, and gently sprayed. To adjust the speckle size, the angle and distance from the sample were manipulated until the ideal pattern is achieved.

For resin tests, a silver permanent ink pen was used to create speckles as spray paint did not show up on the resin. After the sample was formed and relaxed, small dots of silver ink were applied by hand. The dots were made by lightly touching the tip of the marking pen to the resin sample. The size of the dots was difficult to control with this method, and it was essential to maintain very light contact between the pen and the sample when making the dots. If the tip was pressed too hard, it would flatten and applying small dots become more challenging, additionally a dent would be made in the sample. After speckling the samples, it was placed on the heating stage and was ready for testing.

4.2.5 Image Processing and Acquisition

After the camera set up has been calibrated, the temperature cycle set, and the sample prepared the test can begin. The Peltier temperature cycle and the DIC's image acquisition were started at the same time. Images were taken every 30 seconds for the length of the temperature cycle. The images can be processed once the cycle has been completed. The Correlated Solution software imports the images and allows the selection of a section of the image to be evaluated. The subset size is a small area in the selected image with several speckles. In each subset, the software tracks the change in displacement of the speckles and translates the local displacements to the change in strain through the sample.

Strain data over the selected area can be found after processing. In order to eliminate the effects of the edges of the sample strains data is collected by selecting lines that run perpendicular to the direction of the fibre at even intervals down the middle of the sample. The selected stain measurements are then averaged, and the average global strain is found and reported in this work.

4.3 **Results and Discussion**

4.3.1 Resin

A one hold cycle was selected for the resin test for its simplicity. The planned cycle was a 10°C/min ramp from room temperature to 180°C, hold isothermally for 120min and cool to room temperature. The experimental temperature cycle varied from the planned cycle due to the limitation in the temperature control in the Heatcon system. Figure 4.5 shows the recorded temperature of the sample during the cycle. The cure and viscosity profile for this test was predicted by RAVEN simulation software implementing NCAMP material characterization and the recorded temperature data. The profile is presented in Figure 4.6.



Figure 4.5 Resin sample experimental temperature cycle: 10°C/min ramp 180°C hold for 60 minutes, uncontrolled, uncontrolled cool down



It can be seen that the resin does not begin to cure significantly until after 140°C. The viscosity of the resin, on the other hand, decreases dramatically at the beginning of the temperature cycle. Past 120°C the cure begins to increase and the rate at which the viscosity decreases begins to slow.

The resin sample was analyzed using DIC correlated solutions image analysis to find the in-plane principal strain of the sample. The center of the sample was analyzed in order to reduce capturing any inconsistencies the edges of the sample might have induced. Results from the resin sample show a dramatic shrink in-plane as the sample begins to be heated. DIC strain measurements for the principal strain for the in-plane dimension of the sample is seen in Figure 4.7.



Figure 4.7 DIC principal stain data of the resin in-plane. A significant increase in strain begins after 60°C followed by a larger shrinkage. Little change in strain is seen after this point.

The strain results show an unusual response of the material during the heating ramp. The results show an initial expansion followed by a significant shrinkage of the material. It is clear that after 90°C there is a shift from an initial expansion to a large shrinkage. The sizeable negative strain

occurs from around 90°C to 140°C. The principal strain is decreased by 19% in this temperature range.

This principal strain decrease occurs in the heating cycle before any significant cure. Before 140°C the cure would have increased to only 2%. Additionally, the DIC results do not pick up on any significant strain development after around 140°C, despite the development of cure after this point. These trends will be examined further later on in this section.

The DIC analysis software provides data on the change in the height of the sample. The thickness of the sample at the start of the test is 0.30 mm. The average change in height through the test extracted for the sample is added to the original thickness of the sample and shown in Figure 4.8, which compares the height to the temperature through the cycle.



Figure 4.8 Resin sample height development over temperature. Initially the sample grows, shrinking slightly before and during the hold.

The thickness of the sample shows an increase from 0.3 mm to around 0.7 mm as it is heated. Near 90°C the rate at which the sample thickens grows increases until 140°C where it plateaus and

decreases slightly. As with the previously reported strain response, the DIC does not appear to show significant changes in thickness despite curing and thermal effects after the heating ramp. The sample has a Glassy CTE calculated from the height data is approximately 5 x $10^{-6\circ}C^{-1}$ a significantly lower value than expected.

The examination of the sample after processing showed that the thickness of the sample was no longer uniform; the edges (0.70mm) were thicker than the center (0.50mm). Additionally, the sample edges had rounded thus changing the sample from a cylindrical shape to a droplet-like shape.

The surface area of the sample through the temperature cycle was found using ImageJ to analyze images taken at different time/temperature points. This data was plotted and presented in Figure 4.9.



Figure 4.9 Resin sample area change over temperature. There is no apparent expansion in-plane. There is however, a significant shrinkage in the sample as it is heated. Little change in strain is seen after this contraction.

At this stage, the focus of this study will be on understanding the initial response of the material as the primary purpose of this investigation is to understand the pre-gelation behaviour of resin

and later prepreg. Therefore the material response when $\chi > 0.3$ and approaching χ_{gel} is not of interest.

Images of the resin sample during the pre-gelation stage are seen in Figure 4.10. These images are a subset of those used to find the area data that has been presented in the above figure (Figure 4.9). Figure 4.10 provides a visual demonstration of the shrinkage that occurs early on in the heating process.



Figure 4.10 Resin sample during the heating ramp. The majority of strain change occurs during this time. The large change in size occurs between 75°C and 126°C after that point it is difficult to see a significant difference in size.

4.3.1.1 Summary of Resin Test Results and Discussion

The results indicate that different strain, thickness, and area trends occur in the material response during the heating ramp. Table 4.3 summarizes material response within selected temperature zones.

TEMPERATURE [°C]	CHANGE IN CURE	VISCOSITY	IN-PLANE STRAIN	THICKNESS	AREA
20-60	0%	$\downarrow \downarrow \downarrow$	—	↑	—
60-90	0%	$\downarrow\downarrow$	1	↑	$\downarrow\downarrow$
90-120	1%	\downarrow	$\downarrow\downarrow$	$\uparrow\uparrow$	$\downarrow\downarrow$
120-140	1%	\downarrow	\downarrow	↑	—
140-180	12%	—	—	\downarrow	—
↓: Relative decrease in material response					

 Table 4.3 Behavioural Breakdown of Pre-Gelation Resin by Temperature Zone

↑: Relative increase in material response

The in-plane dimensions, strain, and area change, follow similar trends, although the strain does show a notable initial increase that is not seen in the area change. Since the DIC is tracking the movement of the surface, the observed initial strain decrease could be the result of an expansion on the surface that is not seen globally. It is clear for the in-plane dimension, thermal expansion is not the dominating force with the exception of the small increase in strain occurring during initial heating. It does appear that when the viscosity drops due to an increase in temperature, the resin can flow freely, and there is a force that consolidates the in-plane dimensions while increasing the thickness. These effects all occur independently from curing. Figure 4.11 demonstrates this relationship.



Figure 4.11 Temperature driven dimensional changes due to heating. As heat is applied the contact angle between the resin and substrate will increase. The surface tension will draw the resin together while growing to a critical height.

Expanding on this observed phenomenon, it is crucial to consider the effects of surface tension. When the resin is heated, thermal expansion will cause a volumetric expansion. However, due to interface tension, the in-plane dimension does not see this effect initially. When the resin viscosity drops below a specified point (in this system movement appears below 600 Pa s) the liquid will try to minimize the surface energy caused by surface tension. The surface tension of a liquid is the cohesive force between the molecules in a liquid. The surface molecules have an unbalanced force due to the lack of neighbouring molecules and thus try to minimize surface area. Surface tension is highly dependent on the temperature of the liquid, when the temperature increases, the surface energy decreases by pulling the molecules closer together, lowering the surface tension and appearing as a contraction. The effects of surface tension seen in this experiment masks the effect of thermal expansion in this situation.

4.3.2 Prepreg

Initial observation of DIC prepreg results showed a behaviour unlike that proposed by the majority of the literature, but similar to the response seen in the resin samples. As discussed in previous chapters, literature proposes that the material should expand thermally when heated before the cure has developed. However, during the heating ramp, a significant strain drop is observed in the transverse fibre direction of the prepreg for all tests. Test P13 was chosen to represent the typical data set. The strain results are seen in Figure 4.12



Figure 4.12 DIC test on 4 ply sample- P13, temperature cycle 1. (a) Strain vs. temperature plot and (b) strain vs. time plot

This section provides a method for capturing the free strains in the material and seeks to understand the driving mechanisms that lead to the initial shrinking in the pre-gelation state of the prepreg. The gelation point is commonly used to mark a shift in the behaviour of thermoset resins and prepreg as it marks a shift in state. Before gelation resin is a viscous fluid and after the resin acts as a rubbery solid with an increasing modulus. This work further breaks down the behaviour of the material. For the sake of this analysis, each observed change in behaviour is considered a new zone. Additionally this analysis presents test P13 as a representative of the suite of tests done in this work.

The following sections examine the dominant factors influencing the behaviours observed in each of the zones in Figure 4.13.



b

Figure 4.13 Zone breakdown for initial DIC test done on 4 ply sample-P13, temperature cycle 1. (a) Strain vs temperature plot (b) strain vs time plot

The different zones are outlined below:

- Zone 1: Initial Expansion: This zone looks at the initial expansion of the prepreg at the start of the temperature cycle. In this zone, the material is still in the pre-gelation region, and no curing has occurred. This work will quantify the thermal expansion in this zone and offer insight into the physics causing this response.
- Zone 2: Strain Drop: Zone 2 looks at the point where there is a large decrease in strain despite an increase in temperature and a lack of cure advancement. The connection between this behaviour and the changes that occur at the microscopic level will be discussed.
- Zone 3: Curing: This zone examines the conflicting physical effects that cause a null strain response. This area marks the end of the pre-gelation heating ramp.
- Zone 4: Cure Shrinkage: This work quantifies the cure shrinkage response of the prepreg in this section as well as discuss the temperature dependence of the cure induced free strains in the pre-gelation region.
- Zone 5: Post-Gelation Thermal Response: The thermal expansion of prepreg in the glassy state is quantified in this section.

To build up confidence in the test method results we will focus on the post-gelation regions first before diving into the early zones, which differ from the traditional understanding of the material behaviour.

4.3.2.1 Zone 5: Post-Gelation Thermal Response

At the end of the thermal cycle, samples are cooled; at this stage, the composite has cured and behaves like a solid. DIC results show a decrease in strain with the decrease in temperature during the cool down region, which has been marked in Figure 4.14. This relationship can be used to determine the coefficient of thermal expansion in the sample. The relationship is fairly linear as expected.



Figure 4.14 Zone 5 of P13, finding the CTE_{Glassy} base on the cool down region. The linear best fit of the strain and temperature plot was used to find the CTE.

The average linear coefficient of thermal expansion in this region is $33 \times 10^{-6} \, {}^{\circ}C^{-1}$ for 1 ply and $31 \times 10^{-6} \, {}^{\circ}C^{-1}$ for 4 ply samples processed using temperature cycle 1. A breakdown of all the average linear glassy CTEs for each one hold temperature cycle are given in Table 4.4.

TEST NUMBER	TEMPERATURE CYCLE	NUMBER OF PLIES	CTE _{GLASSY} [× 10 ⁻⁶ °C ⁻¹]	AVERAGE CTE GLASSY [× 10 ⁻⁶ °C ⁻¹]	
P2	1	1	34		
P7	1	1	31	33	
P12	1	1	35		
P10	1	4	32	21	
P13	1	4	30	51	
P14	2	4	34	34	
P19	3	4	41	40	
P20	3	4	38	40	

Table 4.4 Direction 2 Linear Glassy CTE Results of DIC Prepreg Tests

The Glassy CTE characterization of AS4/8552 has been reported in the literature to be $33.3 \pm 0.07 \times 10^{-6} \text{ C}^{\circ-1}$ [28], similar to the results found in this study. Constant values suggest this DIC method is appropriate for capturing the strain behaviour of prepreg.

4.3.2.2 Zone 4: Cure Shrinkage

The isothermal hold region is captured in Zone 4. The effect of curing is isolated during the isothermal hold. Figure 4.15 shows the relationship between strain and degree of cure in this zone for a 4 ply sample processed using temperature cycle 1 used to find the cure shrinkage relationship.



Figure 4.15 Cure shrinkage response of 4 ply sample P13 during the isothermal hold at 180°C of temperature cycle 1

Figure 4.15 shows that the cure shrinkage response is non-linear. This nonlinearity is also seen with other trials for this temperature cycle. Studies done on 8552 neat resin have shown the volumetric coefficient of cure shrinkage to be linear [70]. To understand the cause behind this deviation the cure response of Zone 4 was divided into pre- and post-gelation responses. Doing so allows for two coefficients of cure shrinkage (CCS) to be found, the CCS_{pre-gel} and the CCS_{post-gel}.

This is shown in Figure 4.16 for one sample and in Table 4.5, which reports the average pre- and post- gelation cure response for temperature cycle 1.



Figure 4.16 Cure shrinkage coefficients for a 4 ply sample P13 during the isothermal hold at 180°C of temperature cycle 1

TESTTEMPERATURE CYCLEOF OF PLIESCCSpre- GelCLINEAR CCSpre-GelCCSpre- GelCCSpre-Gel GelCCSpre- Gel11	»post- el %]
P2 0.05 -1.13	
P7 1 -0.12 -1.19 -0.21 -1.4	.48
P12 1 -0.56 -2.11	
P10 4 -0.36 -1.15 0.26 1	66
P13 -0.37 -2.18 -0.50 -1.0	.00

Table 4.5 Linear Cure Shrinkage Coefficients for Temperature Cycle 1 of Prepreg

To compare the linear prepreg response to reported cure shrinkage values for 8552 neat resin, simple "rule of mixture" and some underlying assumptions on the material behaviour were used to get an approximate value for the volumetric resin response given the linear prepreg measurements collected in these tests. The following outlines the analysis.

Due to the stiff carbon fibres, it can be assumed that any resin shrinkage in that direction is constrained. Therefore one can assume $\varepsilon_{11} \cong 0$ for unidirectional prepreg. ε_{22} and ε_{33} , are not constrained and are assumed to have approximately the same cure shrinkage. As modulus builds in the resin post-gelation residual stresses are introduced causing the prepreg to experience the Poisson Effect. The global strain change induced by curing is a combination of the Poisson Effect and the cure induced strain in the matrix. The linear response for the in-plane dimensions is shown in Equation 4.1.

$$d\varepsilon_{22} \cong d\varepsilon_{33} = d[(1 + \nu_m) \times \phi_m \times (\varepsilon_{L-CS})_m]$$
4.1

Where ν_m is the matrix Poisson's ratio, ϕ_m is the matrix volume fraction, and $(\varepsilon_{L-CS})_m$ is the linear cure shrinkage response of the matrix. The relationship between the linear and volumetric cure shrinkage behaviour of the matrix can be expressed by the following equation:

$$(\varepsilon_{L-CS})_m = \frac{(\varepsilon_{V-CS})_m}{3}$$
 4.2

With $(\varepsilon_{V-CS})_m$ being the volumetric cure shrinkage response of the matrix. Studies investigating the volumetric cure shrinkage of HEXCEL 8552 have seen a linear correlation between volumetric cure shrinkage and degree of cure [70]. Assuming this linearity, volumetric cure shrinkage is related to a fraction of the total matrix cure shrinkage:

$$(\varepsilon_{V-CS})_m = (\varepsilon_{V-CS})_{m-Total} \times \chi$$
4.3

The degree of cure is represented as χ . The cure shrinkage in the prepreg can be found as a function of the degree of cure and matrix properties by substituting Equations 4.2 and 4.3 into Equation 4.1:

$$d\varepsilon_{22} = d\left[(1 + \nu_m) \times \phi_m \times \frac{(\varepsilon_{V-CS})_{m-Total}}{3} \chi \right]$$
4.4

Equation 4.4 can be simplified, assuming a constant volume fraction post-gelation to the following:

$$d\varepsilon_{22} = V_m \times \frac{(\varepsilon_{V-CS})_{m-Total}}{3} \times \left(1 + \nu_m + \chi \frac{d\nu_m}{d\chi}\right) d\chi$$
4.5

The total volumetric resin cure shrinkage as a function of prepreg linear cure shrinkage after gelation can be found by integrating Equation 4.5:

$$(\varepsilon_{V-CS})_{m-Total} = \frac{\varepsilon_{22} |_{\chi_{gel}}^{\chi_{end}}}{\frac{V_m}{3} \int_{\chi_{gel}}^{\chi_{end}} \left(1 + \nu_m + \chi \frac{d\nu_m}{d\chi}\right) d\chi}$$
4.6

68

A resin volume fraction of 43.1% is reported in the literature and confirmed based on the thickness of a cured ply [91]. The resin volume fraction is used along with simulated Poisson's ratio calculated using RAVEN software. The Poisson's ratio relies on the assumption that the resin bulk modules are constant, and the final Poisson's ration is 0.37 [92]. Given these imputes and using Equation 4.6, the total resin volumetric cure shrinkage $(\varepsilon_{V-CS})_{m-Total}$ is found and reposted in Table 4.6.

Table 4.6 Calculated Total Resin Volumetric Cure Shrinkage				
TEMPERATURE	NUMBER OF	BER OF AVERAGE CALCULATED		
CYCLE	PLIES	VOLUMETRIC RESIN CCS _{POST-GEL} [%]		
1	1	-7.17		
1	4	-9.91		

Mobuchon reported a volumetric cure shrinkage of -9.8% for 8552 neat resins [70]. The average volumetric resin CCS_{post-gel} found it this work is similar to that found by Mobuchon. The 4 ply samples have a slightly higher average volumetric resin CCS_{post-gel} when compared to the 1 ply average.

4.3.2.2.1 Effect of Temperature on Cure Shrinkage

The previously mentioned study done on HEXCEL 8552 resin showed the linear dependence of liquid resin and degree of cure [70]. Initial observations of the nonlinearity of the cure relationship seen in Figure 4.16 raise the question: what happens in the prepreg pre-gelation that could lead to this odd behaviour? To explore this nonlinearity further, several different hold temperatures were examined. The temperature cycles 1, 2, and 3 all have differing hold temperatures 180 °C, 150 °C and 120 °C, respectively. Cycle 3 has a longer hold time than the other cycles allowing the cure to progress to a similar endpoint to the other higher temperatures cycles. Figure 4.17 shows the resulting cure shrinkage. As with samples held at 180°C, there was an observed transition at the point of gelation. However, the CCS increases pre-gelation with lower temperatures.



Figure 4.17 The pre-gelation coefficient of cure shrinkage varies based on hold temperature- Test P13, cycle 1: 3C/min to 180 hold for 120 min cool at 3C/min. Test P14, cycle 2: 3C/min to 150 hold for 120 min cool at 3C/min. Test P19, cycle 3: 3C/min to 120 hold for 240 min cool at 3C/min. CCS was found by taking the linear fit of the pre- and post-gelation sections of the curve. Post-gelation the rate of cure shrinkage increases.

Several variables are affected when the hold temperature changes, higher temperatures initially result in lower resin viscosity while the cure progresses faster. At lower temperatures, the cure progresses much slower and the viscosity is higher. The resins ability to move the fibre bed is connected to its viscosity, higher viscosity resin can pull the fibre bed more easily.

4.3.2.3 Zone 3: The Conflicting Effects of Thermal Expansion and Cure Shrinkage

All regions before the hold are in the pre-gelation region. Behaviour in these regions is therefore more complicated. In Zone 3, the sample is exposed to increasing temperature and an increase in cure for temperature cycle 1. Simple free strain models typically used to predict composite behaviour indicate that the part should be expanding thermally, while the rate of expansion is reduced with the development of a cure.



Figure 4.18 Zone 3 for sample P13. Little change in strain is seen after 130°C. Cure starts developing at about 106°C and the rate of curing begins to increase at around 125°C.

Conversely, the observed behaviour pictured in Figure 4.18 shows little change in strain during this period. Due to the mixed-effects, it is difficult to pinpoint the exact cause of this dulled response. The limited observed strain may be the result of the resin's ability to flow and expand on the micro-level in the pre-gelation phase while being unable to affect the macroscopic scale. Additionally the viscosity of the resin is so low that on the surface of the ply the resin will shear instead of push the fibre bed. The tendency of the rein to shear around the fibres at low viscosity is also responsible for the dampened response seen during the beginning of the hold.

4.3.2.4 Zone 2: Strain Drop

The second zone begins at the transition point between the period of positive strain as the material expands thermally and the shift to a negative strain rate. The zone ends as curing begins. At this point, the viscosity increases and the observed strain begins to flatten (Zone 3). For this sample

P13, the change in strain is -1.34 and occurs between temperatures of approximately 40° C and 105° C for a 3° C /min ramp seen in Figure 4.19.



Figure 4.19 Shrinkage due to core saturation results in Zone 2 for test P13. The observed stain drop occurs between 35°C to 105°C.

The average reduction in strain observed in this zone is -3.58% for 1 ply samples and is -1.39% for 4 ply samples observed between 35°C to 105°C. Figure 4.20 shows the range of shrinkage.



Figure 4.20 Average shrinkage in Zone 2 for 1 and 4 ply samples. There is higher variability in the 1 ply samples compared to 4 ply samples where multiple plies can even out some of the variability of the material.

This shrinkage behaviour is counterintuitive and conflicts with current free strain model predictions. Typically one would expect an expansion when heating the material. To understand why the results from this study are different from the previous assumptions, it is valuable to break down the problem into components.

As the sample heats the thermal expansion effect on resin and fibres is present; however, there is an additional effect on the microscopic scale inside the ply. As seen in Chapter 3, SEM saturation tests, void spaces in the material have an impact on the behaviour. As the resin viscosity drops, the resin starts to flow into the void spaces and draws the material consolidating the ply. SEM imaging only captures a consolidation in the through-thickness direction in areas with high void content. However, the effects of surface tension would be applied to all directions and would be visible in direction 2 as there is no resistance to movement.

4.3.2.5 Zone 1: Initial Expansion

During the initial heating ramp of the material, the prepreg is heated at a rate of 3° C/min from - 5° C, the prepreg expands until $30\pm 5^{\circ}$ C at which point the strain rate shifts and becomes negative leading into Zone 2. Zone 1 focuses on the initial expansion of the material. Figure 4.21 shows a plot of Zone 1 for a 4 ply sample processed using temperature cycle 1.



Figure 4.21 Zone 1 for test P13 where Tg < T. The CTE value (taken as the slope between -3.5°C and 25° C) is 89 ×10-6 °C-1 found by taking a linear fit to this section of the plot.

For 8552, the initial Tg of the material is close to -7° C and increases as the material is heated. The sample temperature stays above the Tg for this period therefore the liquid CTE can be found. Between 1 and 4 ply tests, there was a little variation in CTE_{Liquid}. The average CTE for 1 ply sample was 89 ×10⁻⁶ °C⁻¹ and for 4 plies 89×10⁻⁶ °C⁻¹. This value is lower than the literature reported values for unidirectional AS4/8552 prepreg. The reported linear liquid CTE values range from 256.9 ×10⁻⁶ °C⁻¹ to 373 ×10⁻⁶ °C⁻¹[70,71,80](due to the difference in reporting CTE values the range is large see Section 2.7.8). The results from this test are conservative as the areas of expansion before the strain rate begins to decrease is small.

4.3.2.6 Pre-Condition

Through the course of this study, the ability to remove the effects of surface tension was questioned. As seen in the saturation tests discussed in Chapter 3, prepreg will self-consolidate due to surface tension if given time and held at a temperature which maintains a low enough resin viscosity. With that in mind, a hold step was added to "pre-condition" the material and reduce the void spaces by encouraging capillary induced resin flow to occur. By pre-conditioning the material and allowing the saturation early on, one would hope the effects could be removed and the traditionally pictured strain cure would be seen in the next step of the cycle. The first hold increased form -5°C to 100°C at 3°C/min and held was there for 30 minutes. SEM saturation tests discussed in Chapter 3 showed holding the sample about 80°C for longer than 15 minutes would be enough to saturate the core. Based on the results presented in Chapter 3 the selected pre-conditioned step should reduce the viscosity and allow enough time for the ply to saturate without advancing the cure significantly. After ramping back down to -5°C completing step one, step two begins. Step two is the main cycle and fallows the same temperature cycle as cycles 1, 2, and 3 (3°C/min ramps to varying hold temperatures). The varying second hold temperatures allow the CCS_{pre-gelation} to be compared for different temperatures as done for the one hold tests presented earlier in this chapter. The temperature cycles are shown in Figure 4.22, Figure 4.23, and Figure 4.24.



Figure 4.22 Two Hold Cycle: Ramp from -5°C to 100°C at a rate Of 3°C /min. Hold isothermally at 100°C for 30min. Ramp down to -5°C at 3°C /min. Ramp from -5°C to 180°C at a rate of 3°C /min. Hold isothermally at 180°C for 120min. Ramp down to -5°C at 3°C /min. Curing does not develop significantly until the second hold.



Figure 4.23 Two Hold Cycle: Ramp from -5°C to 100°C at a rate Of 3°C /min. Hold isothermally at 100°C for 30min. Ramp down to -5°C at 3°C /min. Ramp from -5°C to 150°C at a rate of 3°C /min. Hold isothermally at 150°C for 120min. Ramp down to -5°C at 3°C /min. Curing does not develop significantly until the second hold.



Figure 4.24 Two Hold Cycle: Ramp from -5°C to 100°C at a rate of 3°C /min. Hold isothermally at 100°C for 30min. Ramp down to -5°C at 3°C /min. Ramp from -5°C to 120°C at a rate of 3°C /min. Hold isothermally at 120°C for 240min. Ramp down to -5°C at 3°C /min. Curing does not develop significantly until the second hold and do to the low hold temperature there is a gradual increase in cure compared to other temperature cycles.

The results for 4ply samples tested with the pre-cycle step are presented the flowing figures;



Figure 4.25 P22- Direction 2 linear strain response over the temperature of a 4 ply prepreg sample, saturation test with temperature Cycle 5.



Figure 4.26 P22- Direction 2 linear strain response over time of a 4 ply prepreg sample, saturation test with temperature cycle 5.



Figure 4.27 P16- Direction 2 linear strain response over the temperature of a 1 ply prepreg sample, saturation test with temperature cycle 6



Figure 4.28 P16- Direction 2 linear strain response over time of a 1 ply prepreg sample, saturation test with temperature cycle 6.



Figure 4.29 P17- Direction 2 linear strain response over the temperature of a 4 ply prepreg sample, saturation test with temperature cycle 6



Figure 4.30 P17- Direction 2 linear strain response over time of a 4 ply prepreg sample, saturation test with temperature cycle 6.



Figure 4.31 P23- Direction 2 linear Strain response over the temperature of a 4 ply prepreg sample,

saturation test with temperature cycle 7



Figure 4.32 P23- Direction 2 linear strain response over time of a 4 ply prepreg sample, saturation test with temperature cycle 7.

All tests showed repeatable responses. The pre-conditioned step did show saturation, but the strain response on the second step was different than what was expected. The following sections break down the pre-conditioned sample response.

4.3.2.6.1 Step 1: Pre-Conditioning the Sample

During this initial step, the material shrank significantly, but like the previous one hold cycle tests, there was an initial expansion that occurred between approximately -5° C and 25° C. For 4 ply samples, the average liquid CTE found in this area was $87 \times 10^{-6} \, {}^{\circ}$ C⁻¹. This compares well with the reported average liquid CTEs found in Zone 1 of the one hold cycle tests (Temperature cycles 1-3).

Similar to Zone 2 in the one hold cycle test, the initial expansion was followed by a significant strain drop. As the first hold step at 100 °C was achieved, the sample continued to show signs of shrinkage.

TEST	TEMPERATURE CYCLE	NUMBER OF PLIES	DROP IN STRAIN [%]		
			RAMP (START 25°C)	HOLD	TOTAL
P16	6	1	1.54	0.18	1.73
P22	5	4	2.88	0.716	3.68
P17	6	4	1.78	0.69	2.51
P23	7	4	0.76	0.15	0.92
	Average 4	4 ply	1.81	0.52	2.37

Table 4.7 Direction 2 Linear Drop in Strain for Two Hold Cycle Tests

Table 4.7 shows the breakdown of shrinkage over the ramp and the hold. For the 4 ply samples, the average total drop in strain during the first hold is 2.37%. This value is slightly higher than the average seen in the one hold cycle. A higher average strain is due to the increase in the time allowed for the resin to flow. In this pre-conditioned test set up, there is a more extended period where the resin viscosity is low enough to allow flow. Additionally, the variation in strain drop between tests could suggest the variation in prepreg morphology between samples. Some samples having larger regions of dry core than others.

Examining the strain over time plots (Figure 4.26, Figure 4.28, Figure 4.30, and Figure 4.32) it was seen that during the fist hold, strain starts to drop quickly, but begins to flatten towards the end of the hold. This trend shows that the capillary driven infiltration is decreasing as voids are being filled toward the end of the hold. It is reasonable to assume based on this observation that the sample is close to fully saturated.

The cool down ramp during the first step offered a second instance to capture the liquid CTE in the pre-condition stage. The average 4 ply sample CTE_{Liquid} was $70 \times 10^{-6} \,^{\circ}C^{-1}$.

TEST	TEMPERATURE CYCLE	NUMBER OF PLIES	CTE [× 10 ⁻⁶ °C ⁻¹]
P16	6	1	64
P22	5	4	83
P17	6	4	69
P23	7	4	58
	4 ply Average		70

Table 4.8 Direction 2 Linear CTE_{Liquid} Taken From the First Cool Down Portion for Two Hold Cycles Tests

In comparison to the liquid CTE taken from the initial heating ramp, this average was lower, but still within range of the values reported for the one hold cycles. The slightly lower CTE could be due to the slight difference in cure between the first ramp and this first cool down.

4.3.2.6.2 Step 2: Main Cycle

The main step of the test was the same as the previous one temperature cycles. In these two hold tests the second heat up ramp was expected to behave as the literature predicted due to the elimination of the surface tension. Examining the results, however showed there is still a clear difference between theory and reality. The material response showed that on the heating ramp, although there is no shrinkage, there is also no significant expansion. Table 4.9 breaks down the coefficient of thermal expansion reported before 25°C and from 25°C to the hold, as there is a significant change in slope at approximately 25°C.
TEST	TEMPERATURE CYCLE	NUMBER OF PLIES	CTE [× 10 ⁻⁶ °C ⁻¹] BETWEEN -5°C AND 25°C	CTE [× 10 ⁻⁶ °C ⁻¹] BETWEEN 25°C AND THE HOLD
P16	6	1	74	15
P22	5	4	86	15
P17	6	4	80	11
P23	7	4	71	12
	4 ply Average		79	12.8

Table 4.9 Direction 2 Linear CTE_{Liquid} Taken From the Second Ramp Portion for Two Hold Cycles Tests

The first part of the second heating ramp shows the same CTE value as observed during the cool down, as the prepreg is heated the CTE is much lower. As there is no cure progression when this deviation occurs the mechanism driving this change is unclear. An in-depth study of the difference in heating and cooling CTE_{liquid} is presented at the end of this section.

When the hold period is reached during the main cycle, the samples shift between pre- and postgelation CCS as with the past one hold tests. Table 4.10 displays the pre- and post-gelation CCS for the 4 ply samples for the two hold temperature cycles.

Figure 4.33 shows the temperature variation. The response is similar to that seen in Figure 4.17.

TEST	TEMPERATURE CYCLE	NUMBER OF PLIES	CCS pre- gelation [%]	CCS post- gelation [%]
P16	6	1	-0.24	-1.1
P22	5	4	-0.67	-1.7
P17	6	4	-0.56	-1.1
P23	7	4	-0.82	-1.56
	4 ply Average		-0.68	-1.45

4 ply- Pre-Conditioned Test, Varrying Hold Temperatures 0.8 hold at 180°C CCS: -0.70% hold at 150°C 0.7 hold at 120°C 0.6 CCS: -0.57% 0.5 Transverse Strain (%) 0.4 CCS: -1.70% CCS: -0.81% 0.3 CCS 1.7 0.2 0.1 Gelation point -1.5 0 . -0.1 0.5 0.2 0.3 0.4 0 0.1 0.6 0.7 0.8 0.9 DOC

Figure 4.33 Pre-gelation coefficient of cure shrinkage varies based on hold temperature for pre-conditioned tests. P22 was held at 180°C, P17 was held at 150°C, and P23 was held at 120°C

On the cool down ramp after the second hold, the CTE_{Glassy} is found. The average 4 ply CTE_{Glassy} was $32.17 \times 10^{-6} \,^{\circ}C^{-1}$, similar to that found in the one hold tests and reported in the literature. Table 4.11 gives the results for each test.

TEST	TEMPERATURE CYCLE	NUMBER OF PLIES	CTE GLASSY [× 10 ⁻⁶ °C ⁻¹]
P16	6	1	32.7
P22	5	4	30.0
P17	6	4	28.2
P23	7	4	38.3
	4 ply Average		32.2

Table 4.11 Direction 2 Linear CTE Glassy of Prepreg

4.3.2.7 DIC Strain Map Analysis

The DIC produces strain maps as well as average strain values for a sample. The strain is displayed as a 2D or 3D plot on the surface of the prepreg. By examining the way the strain is distributed on the sample some insight into the local mechanisms occurring during processing. Several samples were examined (P7, P8, P12, P13, P14, P16, P17, P18, P22) and similar results were seen. Studying the strain maps it is clear that a UD sample does not experience uniform strain through the curing process and that the ply varies in height. Several points on the heating ramp for test P13 are presented in Figure 4.34. A full video of the DIC results for test P13 can be found in the supplementary material attached online to this thesis (Video 1). The DIC surface plots show early on the strain is uniform (seen as solid orange colour). As the sample is heated the strain is no longer uniform, this is seen as bands of different strains (DIC plots show bands of a different colour) appear. In plots that show times when samples that have high strain variation, such as at 160°C, there are strains as large as -5% (seen as dark blue on the DIC plots) and strains of 1 % (seen as red).



Figure 4.34 DIC strain maps for test P13, 4 ply sample processed with temperature cycle 1. The variations of transverse strain are shown, non-uniformity begins after 50.5°C. Some localized strain is double the average strain. The average strain plots have been broken down and analyzed in Sections 4.3.2.1-4.3.2.5.

The sample profile can also be observed during processing using DIC. A close study of the results showed that from the moment the sample was placed on the tool the height profile was set. A large scale relaxation of the sample does occur within the first 20 minutes of heating on the 3°C/min ramp, flattening any large deformations in the part. Despite the larger scale relaxation, the mesostructure was not altered. It is reasonable to assume that what was observed is the variations of the prepreg structure.

Examination of the DIC strain map showed uniform strain disputation early on and the average strain shows a positive expansion. As discussed previously the dropping viscosity leads to capillary driven resin flow into voids. Variability in ply morphology causes resin flow relative to the fibre bed to be variable, and assuming strain is connected to the changes in resin this morphology variability leads to variable local strains.

An additional observation on the magnitude of strain variability was made. There are zones where the strain is doubled (or more) and zones with close to no strain. When comparing 1 and 4 ply samples, the 1 ply sample showed higher variability in magnitude, although both layups show similar frequencies in stain variation. This is constant with previous finding which stated multiple plies dampen the ply saturation induced strain drops.

4.3.2.7.1 CTE Comparison Using DIC Strain Plot

The discrepancy between heating and cooling CTE discovered in the two hold cycle tests was not expected. To evaluate the cause, DIC strain maps were studied for any variations in the strain that could cause the global response presented previously in this chapter. An in-depth study of sample P22 a 4 ply UD lay up sample processed using temperature cycle 5 was preformed. The results presented in these tests were representative of the other DIC tests.

To evaluate the evolution of strain in the sample as it was heated, several points through the heating cycle, all pre-gelation, were studied. Figure 4.35 shows the strain and temperature plot for this test marked with key points.



A 3D map of the transverse strain in the sample was evaluated at each of the test points. The strain in samples was found using the start of the hold as the reference point. The sample is seen in 3D with the fibre direction running along the Y-axis. Video files in the attached supplementary material shows the progression of strain and the sample in space (Video 2, Video 3, and Video 4).

During the initial hearing ramp the CTE_{Liquid} is observed in Zone 1, between -5 °C and 25 °C. After 25° C the average transverse strain transitions, beginning to shrink as the capillary force draws resin into the prepreg (See sections 3.3 and 4.3.2.4 for a thorough discussion on this mechanism). The DIC strain maps for this zone showed a shift in strain distribution at the same time point. This shift is observed as a transition from small, seemingly random variations in strain to larger strain variations occurring in bands running in the direction of the fibres. Figure 4.36 shows several points along the ramp (A, B, C, D, and E) all strain maps have been scaled to best display variations in the strain pattern.



A 5 min 9.86 °C

B 10 min 24.9 °C

C 20 min 54.9 °C



Figure 4.36 Strain maps showing local variations in strain as the prepreg is heated initially. The reference point for these tests is at the start of the test. Points A and B do not show large variations in strain but C thought E show larger strain variations.

Between B and C there is a transition from random strain distribution to a patterned distribution of strain, as mentioned. This point corresponds with the point where prepreg stops responding as expected. Before this transition the global strain is expanding with a linear CTE_{Liquid} of 102×10^{-6} °C⁻¹. After these bands of variability strain increase as the temperature is increased and the average strain begins to shrink. The local and global strain trends continue throughout the hold.

It is expected that at the same viscosity and temperature the prepreg should respond the same and, when in the liquid region, the CTE values should be similar. However, that average CTE_{Liquid} on

the cool down ramp of the first hold $(83 \times 10^{-6} \,^{\circ} C^{-1})$, although similar to the CTE value measured during the first heating, does not match the CTE_{Liquid} of the heating ramp for the second hold. Up until 25° C the cool down and heat up show the same trend in the average transverse strain response $(86 \times 10^{-6\circ} C^{-1})$, but after that point the second heating ramp shows a much lower response, by 50°C this deviation is apparent and by 100°C the CTE on the second heating ramp is close to zero. To examine the difference between cool down and heat up CTE DIC strain maps at corresponding temperatures were compared. When the sample is saturated a large strain drop occurs and masks any smaller variations in strain that occur after that point. For that reason the reference point used to determine the strain was changed. Instead of referring to the start of the test this portion of the analysis uses the start of the second heating ramp, point A', as the reference point. The following figure compares the cooling and heating ramp side by side demonstrating the differences in strain evolution.









Е"

135 min

100 °C



F'' 150 min 145 °C



G" 162 min 180 °C

Figure 4.37 Using the end of the first step as a starting point key points are compared for the cool down ramp and the second heat up. This view shows how different the strain profiles are for heating and cooling. Looking at the local variations in stain helps to explain the samples overall behaviour. At point D' and D'' the variations become clear. With the cool down there are small random variations in strain the heat up has localized regions of higher and lower strain after approximately 50°C.

Comparing the cool down to the second heat up ramps it becomes clear that there is a difference in the strain distribution. Similar to the first heat up, thermal expansion was observed and behaved as expected for the cool down region. During this region the strain maps show a mostly uniform strain pattern with only small random variations. The strain pattern indicates that the prepreg moves as one unit, contracting evenly in all areas. The second heating ramp shows deviation from the random strain variation pattern occurring at the same point the average strain response varies from the expected expansion. As the prepreg is heated some sections of the material appear to try and respond as expected, for example F'' and G'' show peaks with strain values at/or above 1%, matching what the average strain response should be if the material had appropriately expanded. Although some areas on the prepreg expand at the expected magnitude, the majority of the material lags, and thus the average strain response is dampened dramatically.

The difference in strain between the cool down ramp and the heating ramp was calculated and the strain maps are presented in Figure 4.38 below. This visualization helps identify the regions that begin to lag. Note the scale has been changed to accurately display the variations in the prepreg.





Figure 4.38 Calculated difference between cool down strain and second heating ramp strain for key points. For three different temperatures the transverse strain form the second heating ramp was subtracted from the cool down ramp. By doing this the locations where the heating ramp is lagging behind the cooling is seen. At 50°C (E' and E'') there is very little lag. At 70°C (D' and D'') show larger variance (areas of more green (Δ .25% strain) appear). By 100°C there is large variation up to at least 0.5% difference in strain between the cooling and heating.

There are several important conclusions concerning the difference between cooling and heating on the values of CTE_{Liquid} . First and foremost, it should be noted that although the strain behaviour becomes localized during the heating cycle there is no localized deformation or buckling in the sample spatially. The microstructure profile of the sample is set early, and the peaks and valleys of the prepreg stay constant.

The second is a possible cause for this difference. This researcher proposes the difference in CTE comes from the difference in stress states the resin is under between the cooling ramp and the heating ramp. When cooling resin wants to contract and pulls on the fibres to follow. By doing this the resin is put into tension. While in tension the resin molecules will continue to pull the fibres closer together and the global thermal contraction of the ply is observed. For heating the global response is dampened. This is because the resin is in compression while trying to push the fibres outward. When in compression and the viscosity is low enough the resin will bend or shear around the fibres as opposed to pushing them. At this time is difficult to prove exactly what is happening in this area however, the theory presented here is the best description at this time. A schematic of this relationship if present in Figure 4.39.



Figure 4.39 Schematic representing stress states resin is up under when heated and cooled. When cooling the resin pulls on the fires as a result the resin feels a tensile force. When heated the resin wants to expand and pushes on the fibres resulting in a compressive force induced on the resin. As the liquid resin does not like to be in compression it shears or bends around the fibres. At the level of the ply this state leads to no apparent strain change.

4.4 Summary of DIC Tests Results and Discussion

A method using DIC to capture the free strains in resin and prepreg material enables researchers to visualize behaviour before gelation. Results from neat resin DIC test provide valuable information on the average resin behaviour. As heated, lowering the viscosity, uncured resin will shrink inwards in-plane and expand through thickness. This behaviour is in accordance with the in-plane consolidation effect caused by surface tension. It is important to note that thermal expansion was not noticeable during this time. The surface tension effects are stronger than the thermal expansion effect.

DIC tests performed on prepreg highlight the importance of the resins pre-gelation behaviour. The results differ from what literature dictates is expected. Throughout the analysis of the results confidence is built in the validity of this test method, initially looking at the post-gelation response, which is well understood. Chapter 3 showed the significant effect capillary driven saturation had on consolidating a ply through thickness. This consolidation is seen again in the average in-plane strain before gelation. Additionally, this work looked at local variations in free strain on the sample. It was seen that the transition between uniform strain behaviour and localized variations which occur at the same point the average global strain behaviour differs from the predicted response. By combining the knowledge gained about the bulk movement of resin and the knowledge of resin fibre interaction as prepreg is heated, this work broke down and explained the response of the material concluding the pre-gelation material behaviour can not be explained using solid mechanics.

Working backward from the post-gelation region to the uncured material the following conclusions from each zone are listed below;

Zone 5: Thermal Contraction. The average behaviour seen in UD prepreg samples is consistent with values reported in literature. This work found that averaging tests of varying layups ([0]₁ and [0]₄) tested with a variety of temperature cycles to be 33× 10⁻⁶ °C⁻¹. A breakdown of the tests can be found in Table 4.12

• Zone 4: Cure Shrinkage. The prepreg showed a non-linear response to curing instead of the expected linearity. There is a transient between the pre- and post- gelation response. Before gelation the effect of cure is dampened resulting in lower CCS compared to those reported after gelation. The linear CCS pre-gelation for all tests averaged to -0.6 and the average CCS post-gelation was -1.6. The post-gel CCS was consistent with the literature.

In addition to seeing a shift between pre- and post- gelation this work found that by lowering the isothermal hold temperature, the impact of cure on the strain was higher compared to higher hold temperature tests. Given more time at a viscosity that is low enough to allow resin flow, the material will experience the effects of cure shrinkage. The response pre-gelation suggests that resin at low viscosities will shear instead of move the ply. Lower temperatures have higher resin viscosities and therefore have a larger effect on the ply shrinkage.

- Zone 3: Conflicting Effects of Thermal Expansion and Cure Shrinkage. In this time the sample is exposed to changing heat and the cure reaction has begun. Results showed very little strain response in this zone. This null response could have been a result of resin movement on the micro-level that did not have an effect on the larger scale. Alternatively the response could have been caused by the resins desire to shear across the fibre bed, as opposed to moving the fibres, due to the low viscosity , in this zone.
- Zone 2: Shrinkage. The microscopic examination of resin and fibre interaction discussed in Chapter 3 concluded that the capillary pressure induced by the surface tension of the resin was enough to draw the resin into the core of the fibre bed. As the resin saturated the core of the material, the ply itself was also drawn close together in the through-thickness direction. In the macroscopic tests discussed in this chapter, the surface tension effects were seen in the neat resin, where the sample shrank considerably in-plane, and grew in height conserving volume. Understanding the microscopic response, it is even more apparent that self-consolidation in the ply is expected. The prepreg response did follow this behaviour. The shrinkage response due to surface tension seen in Zone 2, demonstrates the strength of this effect as it counteracts any thermal expansion that the prepreg would also

be experiencing at this time. The average of varying layups ($[0]_1$ and $[0]_4$) tested with a variety of temperature cycles test showed an average shrinkage of -2.0%.

This work found pre-conditioning of prepreg by adding in an additional low-temperature hold before the main cycle allows the ply saturation to occur early on. However, the removal of this effect did not cause the material to respond as literature proposes. Both the one hold and the two hold cycles saw low expansion after the prepreg had been saturated, suggesting that the surface tension alone is not the only effect missing from the simple free strain model. As with Zone 3 some possible causes for the low strain response could be micro-scale resin movement that can not be captured at a large level, or shearing. For the two hold test, the difference between the CTE values taken for the same DOC on the cool down and heat up showed that, at the deviation point, the strain begins to vary locally. One possible explanation for the differences in CTE values comes from resin to respond to different stress states. On the cool down ramp the resin experiences a tensile force and is able to move the fibres. The resin is in compression on the heating ramp and will shear around the fibres as opposed to moving them.

Zone 1: Initial Expansion. At the start of each test there is expansion as the sample is heated. For all tests the average 89 ×10-6 °C⁻¹ for 1 ply and 89×10-6 °C⁻¹ for 4 plies. The literature reports linear CTE_{Liquid/Rubbery} values ranging from 74 ×10-6 °C⁻¹ to 373 ×10⁻⁶ °C⁻¹ [70,71,80](see Section 2.7.8 for an explanation of range.) The initial expansion CTE is within range.

Given these zones, what once appeared to be a complex response that contradicts literatures expectations of pre-gelation behaviour can now be understood. The DIC method provided a non-contact technique to track strain development in prepreg and resin unlike most of the previous techniques. The following tables summarizes the prepreg material free strain response captured using DIC. Figure 4.40 presents all the one hold tests together to highlight the repeatability of these measurements.



Figure 4.40 One hold temperature cycles tests. 1 ply tests are marked with a dashed line. 4 ply tests are marked with a solid line. All tests are zeroed at the end of the temperature hold step. 1 ply samples have higher stain drop initially than 4 ply samples

Test	Temperature Cycle	Number of Ply's	CTE _{Liquid} [× 10 ⁻⁶ °C ⁻¹]	Surface Tension Induced Strain Drop [%]	Linear CCS _{pre-} gelation [%]	Linear CCS _{post-} gelation [%]	CTE _{Glassy} [× 10 ⁻⁶ °C ⁻¹]
P1	0	[0]1		Т	est Failed		
P2	1	[0] ₁	95	-4.13	0.05	-1.13	33.6
Р3	1	[0]10	Те	st Failed- Po	or Temper	cature Cont	trol
P4	1	[0]20	Те	st Failed- Po	or Temper	ature Cont	trol
P5	1	[0] ₁	Tes	t Failed- Ter	mperature	Stopped E	arly
P6	1	[0/90]4	Tes	st Failed- Ter	nperature	Stopped E	arly
P7	1	[0] ₁	97	-4.02	-0.12	-1.192	30.9
<u>ت</u> P8	1	[0]4	Te	st Failed-Ten	nperature	Stopped Ea	arly
64 Cyc	1	[0]4	Tes	st Failed-Ten	nperature	Stopped Ea	arly
P10 Be Hol	1	[0]4	89	-1.46	-0.36	-1.15	32.2
О́ Р11	1	[0/90]4	Test Failed-no significant in-plane strain changes, can not distinguish from DIC noise				
P12	1	[0]1	75	-2.60	-0.56	-2.11	34.5
P13	1	[0]4	89	-1.34	-0.37	-2.18	29.6
P14	2	[0]4	91	-0.99	-0.69	-1.73	33.67
P15	2	[0] ₁	Tes	st Failed-Ten	nperature S	Stopped Ea	arly
P18	4	[0]4	76	-1.68	-1.12	-	72.99
P19	3	[0]4	86	-1.53	-0.91	-1.56	41.01
P20	3	[0]4	70	-1.36	-0.88	-1.63	38.23

 Table 4.12 Summary of All DIC Prepreg Tests- Free Strain Analysis Breakdown

	Test	Temperature Cycle	Number of Ply's	CTE _{Liquid} [× 10 ⁻⁶ °C ⁻¹]	Surface Tension Induced Strain Drop [%]	Linear CCS _{pre-} gelation [%]	Linear CCS _{post-} gelation [%]	CTE _{Glassy} [× 10 ⁻⁶ °C ⁻¹]
Two Hold Cycle	P22	5	[0]4	102/83/86	-3.68	-0.7	-1.70	30
	P16	6	[0] ₁	79/64/74	-1.73	-0.25	-1.10	32.74
	P17	6	[0]4	81/69/80	-2.51	-0.57	-1.72	28.23
	P23	7	[0]4	77/58/71	-0.92	-0.81	-1.57	38.29
		Averages		81	-2.0	-0.6	-1.6	33
		Standard Deviation		10.9	1.2	0.3	0.5	14.3

Chapter 5: Variably in the Structure of a Ply

5.1 Introduction

While exploring the pre-gelation state of prepreg this work showed the connections between the global strain response and localized changes in strain. Previously the connection between variations in the morphology of the ply (location of void, variation in high etc.) was discussed for the one and two hold tests. Several significant outcomes came out of that discussion. It was seen that the height profile of a sample is set from the start and strain localizes when capillary flow is present. This section continues to explore the local variations in strain and height across a one ply prepreg sample by comparing these variations to the internal morphology of a ply. To explore the internal morphology, SEM imaging is used to identify the resin and void distribution through a ply cross-section. Additionally, Optical Microscopy and Infrared (IR) thermography examined the surface of the uncured ply identifying the distribution of resin on the surface.

5.2 Methods

5.2.1 Material

As with the previous study on the micro-response of composite material, this study continues to focus on Hexcel AS4/8552UD prepreg material [79]. Previously characterized cure kinetics and viscosity models for the prepreg system are implemented in RAVEN simulation software [83,84] and used in this study.

5.2.2 DIC Methods

DIC set up, and the camera calibration for this experiment was the same as the resin and prepreg tests presented earlier in Chapter 4. Images were taken every 30 seconds during the test, and after completion, Correlated Solutions software was used to analyze the sample. In-plane strains and the change in the height (z-displacement, Δz) of the sample was calculated by the software based on the deformation of the speckle pattern.

The heating system used in this test was the Anton Paar Peltier heating plate covered with a nonstick Teflon substrate to reduce tool-part interaction [88]. The temperature cycle used was a fast 10°C/min ramp from 20°C to 60°C followed by a 30 minute hold at 60°C before rapidly cooling to 0°C, quenching the sample and halting the resin flow. 1-ply of AS4/8552 prepreg was cut into a 25mm x 25mm x 0.2 mm square sample. A black on white speckle pattern was applied using spray paint as described in the previous section. In addition to the speckle pattern, two sets of three evenly spaced dots were placed 7mm from the top and bottom of the sample. A pin was pushed into the prepreg at the center of the reference dots causing the fibre bed to be disturbed. These dots and pinpoints were used as a reference when making cross-section cuts after DIC images have been taken.

5.2.3 SEM Methods

Once the sample used in the DIC test returned to room temperature, cross-sections of the material were taken using the reference dots placed on the sample. The cross-sections were prepared for SEM imaging in the same manner as discussed in Chapter 3. Samples were cut using a thin sharp blade healed at a 60° angle and edges were cleaned using a piece of scotch tape. Cross-sections were placed in a vacuum chamber overnight to eliminate any off-gassing that could occur in the SEMs pressure chamber. To image the samples were then mounted with carbon tape on a small aluminum block and sputter-coated with gold. A stitched image was taken using an FEI Quanta 650 SEM with an acceleration voltage of 15kV.

5.2.4 Infrared Thermography Methods

Infrared cameras can pick up the emissivity of an object. This study looks at the difference in emissivity on the surface of a ply of prepreg. A FLIR IR camera was used to capture the thermal profile of a 40mm x 40mm x 0.2mm sample of prepreg. The sample was heated from 20°C to 60 °C at a rate of 10°C/min, held at 60 °C for 5 minutes than rapidly cooled. IR thermographs were taken immediately after the temperature ramp. The image was taken approximately 100cm from the sample. FLIR software was used to analyze the sample.

5.2.5 Optical Microscopy Methods

The surface of the same 40mm x 40mm x 0.2mm sample of prepreg used for IR thermography was examined under a digital microscope after it had been cooled. A Keyence VHX-1000 digital microscope was used to capture high magnification images that could be analyzed using ImageJ analysis[87].

5.3 Results and Discussion

5.3.1 DIC

A snapshot of the strain and position a prepreg sample experiences in the middle of the temperature cycle is presented in Figure 5.1. This snapshot was taken 15 minutes into the 60°C isothermal hold, at which point, based on the findings in previous sections, the viscosity of the resin is low enough to begin flowing into the core of the material but not saturate the core.



Figure 5.1: 3D DIC transverse strain map of the sample 15 minutes into the 60°C isothermal hold. The orientation of the ply is marked, the fibres are in the direction of the Y-axis.

The DIC strain map clearly shows the variation of strain through the material ranging from -0.15% to -1% along with variations in height. Close examination of the strain map shows a repeating pattern in Δz . Approximately every 4mm there is a peak in height. A trend repeated in the other

DIC tests discussed previously. A line was selected across the sample using the pinpoints for reference was used to explore the local variations seen in Figure 5.1. This is the same line where the cross-sections were cut from to be examined using SEM discussed later. The strain and height data of the sample can be extracted from the selected line.

Figure 5.2 and Figure 5.3 show the local variations in the strain and height of the sample during the isothermal hold with the start of the test as a reference point from which the strain measurements are taken.





The focus is made on the strain development over the hold because before that point variations (such as expansion in the sample) could be attributed to thermal expansion, but during the hold, variation will come from changes in the prepreg morphology. Additionally, the sample is not expected to cure significantly.

Focusing on the change in height presented in Figure 5.3, there appeared to be a peak in height that was 4 mm long and repeated across the sample. Stewart reported a tow size of 4mm for AS4/8552 found by performing a burn off resin test [20]. The reported tow size value matches the apparent roughness of the material, suggesting the presence of the fibre tow induces the trend observed in Δz . Looking at the global behaviour, it appears that the ply increases in thickness during the hold, although local variations are still present.

Examining the strain variation of the sample seen in Figure 5.2, the frequency of strain peaks is higher than the peaks in height, approximately every 1 mm. Globally the sample follows the expected behaviour discussed in the previous section. When held at an elevated temperature the

prepreg shrinks due to the effects of surface tension driven consolidation. The local variations in the strain signify some regions of the material have more noticeable shrinkage than in other areas. It is reasonable to think the local variations in strain could be indications of differences in the morphology of the ply. Further investigation into the morphology of the sample could inform the cause of this pattern.

5.3.2 SEM

Examination of the prepreg samples cross-section using Scanning Electron Microscopy provides a snap-shot of the prepreg morphology after the heating cycle captured by the DIC test. Insight into the irregularity of the sample can be gained by analyzing SEM images. Resin and void distribution along the sample can be seen in Figure 5.4, a portion of the imaged cross-section.



Figure 5.4: SEM image of a section of the AS4/8552 prepreg sample cross-section after the heating cycle. Black spots are priority in the ply.

The void content can be represented graphically using a Matlab image analysis routine. The code used for this analysis was created by Hubert Courteau-Godmaire [93], a description of this code can be found in Appendix B . The void content is measured in pixel count, and Figure 5.5 shows the frequency of voids along with the sample. The average spacing between large void regions is 1 ± 0.5 mm based on this image analysis.



Figure 5.5 Void content over SEM cross-section. Peaks signify areas of high porosity, dips are areas with higher resin content.

The strain plot does not appear to match with the void content consistently. The human-made voids caused by pinpricks offer insight into the underlying trends. As seen in Figure 5.6, these regions are correlated with regions when the strain changes, or the space between the peak and valley.





Figure 5.6 Comparison of SEM image and strain measurement. Different regions are marked. A is the pinpoint defect placed in the ply as a marker. This section is linked to an areas with higher negative strain. Region B marks a large void. C represents regions of a consistent void distribution. The transition from constant void distribution to a higher or lower void content appears on the strain plot as a peak.

This trend is apparent in the human-made voids (approximately at -7mm, 0mm, and 7mm) and also seen on several occasions. The change in strain appears to signify a change in morphology. When the material transitions from different densities of voids, there is a change in the local strain. This can be seen by looking at the strain at the same location as a human-made void. In this region, marked as region A in Figure 5.6, there is a sharp change in void density, and the strain shows a change occurring at this stage. This is also seen in regions with large void content that occurs naturally in the ply as seen in location B. Regions where there are many voids, but little variation in density does not show a change in strain. These locations are marked as C in Figure 5.6. Although this relationship holds up in most cases, there are points where this statement is false. Due to the small sample size, it is difficult to make statements on the statistical significance of this connection between changes in strain and void areas. Further tests in this area are needed. This test does, however, indicate the potential for a correlation and the benefits of understanding how local strain variations are linked to changes in void content and could have a significant impact on the industry.

5.3.3 Surface Characterization- Microscopy and IR Thermography

Examination of the surface morphology can indicate patterns in the prepreg that could cause the non-uniformity of the local strain and thickness variations of the sample during processing. Figure 5.8 and Figure 5.7 show the surface of a prepreg sample using Optical Microscopy and IR Thermography respectively. In both cases a pattern is visible. The sample examined with these two techniques is cut from the same material, but is not the same sample that was examined in the previous methods.



Figure 5.7: IR thermograph of AS4/8552 prepreg surface heated to approximately 60°C for 5 minutes. Higher emissivity regions are resin-rich areas. A 1 mm spacing exists between regions.



Figure 5.8: Optical microscopy image of AS4/8552 prepreg surface. Higher reflective regions are coated in resin. There is a 1 mm spacing between regions.

In Figure 5.8, the surface shows stripes of resin-rich areas and areas with dry fibres. Spacing between resin-rich areas is found to be approximately 1.1 ± 0.4 mm. This measurement was found using ImageJ [87] measurement techniques.

The IR thermograph seen in Figure 29 shows a similar striped pattern switching from areas of higher and lower emissivity. The resin will have a higher thermal conductivity compared to the fibres and so appear hotter on a thermograph. The spacing between the hotter resin-rich areas and the areas with fewer fibres averages to 1.2 ± 0.5 mm.

5.3.4 Summary of Results and Discussion

DIC, SEM, optical microscopy, and IR all provide a unique look at the initial state of uncured prepreg. In comparing the different results, links between the morphology and the observed behaviours can be made. An examination of the surface quality using IR and optical microscopy showed a pattern in the resin distribution. Both methods observed bands of resin-rich areas spaced 1mm apart. A 1mm spacing was also observed in the strain peaks examined using DIC on a different sample.

Although future work is needed to correlate the strain response to the morphology of a prepreg ply, it is reasonable to assume that they are linked. Comparison of the strain and SEM images showed areas where a change in the morphology triggers a transition in the strain response. In addition to local strain variations in the sample, DIC provided the variation in height over the sample. Repeating 4mm peaks were observed over the sample, which can be linked to the tow size. It seems promising that the non-destructive test methods presented in this section could make these links.

5.4 Summary of Macro Response

This chapter builds upon the results of the previous chapter. Both chapters outlined several techniques for capturing the free strains induced in resin and prepreg during heating. The techniques developed in this work were able to capture the true material behaviour in a way that has not been seen before. This work primarily focused on the pre-gelation behaviour of the material and found that the literature suggested response did not satisfactorily describe the

prepreg behaviour. Results showed that surface tension has a significant impact on the pregelation stage of the material. The findings presented suggest the pre-gelation state should not be expected to behave in the same manner as the post-gelation region. Due to the methods used the differences between expectation and reality in the pre-gelation state are explained. The main points from this work are detailed below.

5.4.1 Pre-gelation effects

The pre-gelation region has not been widely investigated, and therefore, the results presented in this section challenge the anticipated free strain behaviour. This work presents a way to characterize the pre-gelation region without influencing the material through processing. It is important to note that any interaction with the material in this phase has the potential to induce defects or change the final response of the material. The results, both for tests done on 8552 neat resin and AS4/8552 prepreg demonstrated the strong influence the resins surface tension has on the material as well as the importance of temperature on the ability of the material to respond to changes when in a liquid or rubbery state. Both the average and local strain response reflects the point at which the material no longer behaves as literature suggests. The local strain values show distinct regions with more or less strain, while the average strain begins to decrease on the heating ramp due to capillary driven saturation of the core. The same localization occurs when the liquid CTE diverges between the heating and cooling ramps for the same degree of cure. In that case this researcher suggests the differences comes from the stress state the resin is placed in. The low CTE response seen when the ply is heated could be caused by resins shearing when put in a compressive state when trying to expand and push fibres.

The liquid behaviour of resin in pre-gelled prepreg also has an impact on the curing behaviour. The in-plane cure shrinkage response is dampened and the magnitude of the damping effects is dependent on temperature.

5.4.2 Post-gelation

The DIC technique provides a simple, non-intrusive method for capturing the post-gelation behaviour of prepreg. This study found that after gelation the transverse strain response to cure, although not linear at first, begins to shift to a more linear relationship with a coefficient of cure shrinkage close to that reported in the literature. The glassy CTE of the prepreg responds as expected and gives a similar value to the literature. Although the DIC technique provides a clear picture of what occurs post-gelation for prepreg, the response of neat resin is not well captured by this measurement technique. A possible cause could be resin bonding to the substrate. Further development to the testing set up will be needed to investigate this limitation.

5.4.3 Strain and the Ply Morphology

In the world of big data, the more information manufacturers can gain on the product they are making, the better the process can be tailored and improved to reduce defects in the parts. Gaining information early on will increase the effectiveness of these changes. This work looked at the local variations in strain on a ply of prepreg at the start of processing. It seems logical that the structure of the prepreg could be causing strain variations, so cross-sections of the ply were analyzed, and the morphology was compared. SEM cross-sections showed variations in void content along with the sample. Comparing the types of voids (size and density) to the strain variation captured with the DIC it became clear that, although impossible to correlate completely, there are some relationships between the morphology and strain. From this analysis, it appears a change in strain signifies a shift in morphology. Areas with a constant void density are tied to constant strain areas. Shifts between densities, either to a resin-rich or large void area, cause a change in strain.

There are several reasons why the findings in this study are only theories on the connection between strains a morphology. Primarily because of the small data size which does not allow for statistical significance. Another comes from the nature of working with uncured prepreg. Any handling of the uncured ply has the potential to deform the material. Cutting has been proven to be especially challenging and had the potential to change the observed morphology seen in the cross-sections from the original state it was in when examined using DIC. Despite all the limitations and sources of error, this work still opens up the opportunity for future work done on using non-contact characterization techniques to predict defects.

5.4.4 Uncured Prepreg Surface Characterization

This work discussed several non-contact methods that provided information on the texture of the uncured prepreg surface. DIC analysis provides information on the relative change in the height

of a ply as it was heated. The results saw 4mm wide peaks evenly spaced in direction 2, perpendicular to the fibres. This spacing matches the expected tow size of AS4/8552.

Further development of this technique could lead to a non-contact measurement tool for determining the tow size and alignment. Optical microscopy and IR imaging also provide details on the surface of an uncured ply. The distribution of resin on the surface of the ply can be seen using both techniques. The difference in emissivity between fibres and resin shows up when imaging a heated ply and can be used to determine the resin distribution. Visual observation using optical microscopy shows resin-rich areas evenly spaced along with the prepreg sample in the fibre direction.

Both of these methods could be examined and used for quality checks to ensure the resin distribution is correct as resin distribution plays an important roll in the tackiness of the material, which in turn can influence the presence of defects in the forming process. Having a non-contact way to examine the quality of the material that could be incorporated into the factory process as discussed in the strain and morphology section could improve the processing of composite material and reduce the occurrence of defects in the part.
Chapter 6: Conclusions, Contributions, and Future Work

6.1 Summary

In recent years there has been a shift in manufacturing CFRP techniques that makes it more important to understand the initial state of the material. There has been a transition from traditional lay-up to AFP and forming methods. Both of these manufacturing methods involve handling the material in the initial stages of processing. In the initial stage, the raw material is highly susceptible to deformations due to handling. This is because initially, the thermoset resin in the prepreg is in a viscous liquid phase. As the composite is heated, the thermoset resin develops crosslinks between polymer chains to become a solid encasing the fibres. The point at which the resin goes through the transition from the viscous liquid phase to a solid phase is the gelation point. In addition to difficulties handling the prepreg, the pre-gelation state has been seen to influence the formation of defects such as wrinkling, porosity, and residual stresses that become apparent later on in processing. Because of this shift in manufacturing and the connections researchers are finding between the initial condition of the material and the final part quality, a thorough understanding of the pre-gelation regime in the prepreg is needed. With this understanding, micromechanical models can be improved to better represent the behaviour during the pre-gelation phase.

Although there is increasing motivation to study the pre-gelation region, there are limited studies that look in this area. The challenges come from finding a measuring technique that can accurately capture the free strains induced in the material during this phase without influencing the material. Traditional methods to characterize prepreg have difficulties capturing and interpreting the pre-gelation behaviour of the material. This is because at this stage, the material is easily influenced by handling, and most techniques involve some probe which applies pressure to the sample. By developing an approach using a non-contact measurement technique and by performing tests that probe the pre-gelation behaviour, this work was able to demonstrate differences between the assumed and the real material response.

The main objective of this thesis was to explore the free strains in thermoset prepregs with a significant focus on the pre-gelation region. DIC provides a non-contact strain measuring technique that avoided problems seen in traditional strain tracking techniques. Additional tools like SEM, IR thermography and optical microscopy allowed more in-depth exploration into the

morphology of the prepreg. The effect of the resin in its pre-gelation fluid state on the global behaviour of the material was probed using novel methods developed in this study.

This work was performed on Hexcel AS4/8552 unidirectional (UD) prepreg (HexPly AS4 12K/8552; 35%; 190AW) [85] and 8552 neat resin. AS4/8552 prepreg is made using a hot-melt process. During the fabrication process, dry UD carbon fibres are fed through hot thermoset resin. The resin saturates the surface of the fibre bed, leaving a dry core. Some areas in the core of the prepreg are more saturated than others. Regions between tows tend to have higher resin content.

Several different approaches were taken to better understand free strain evolution in the material during simple temperature cycles. The first approach was to examine the resin distribution and flow in a single prepreg ply. Samples of AS4/8552 were examined using SEM imaging after being heated to varying temperatures. Demonstrating the effect the change of viscosity on resin movement within the fibre bed. Two different conditions were examined for each temperature, with and without external pressure (i.e. vacuum pressure). Results showed that in both conditions, prepreg held at higher temperatures would consolidate due to the surface tension driven capillary flow of the resin. This understanding of the microscale was helpful as the focus was shifted to the macroscale.

DIC is a non-contact strain measuring technique that was used in this study to examine both resin and prepreg behaviour on a larger scale than that presented in work done using SEM imaging. The macroscopic, or global response of the material to simple temperature cycles was studied. Resin tests captured the effects of surface tension. After the viscosity dropped to a level that allowed the resin to flow, the sample shrank in the in-plane dimensions while increasing in thickness. This response occurs before the onset of curing. Unfortunately, due to the interaction of the resin and the tool, the post- gelation response was difficult to capture.

DIC tests performed on prepreg also demonstrated the in-plane shrinkage due to surface tension. This method studied the average transverse strain response of unidirectional prepreg. This response was not expected or reported in the literature but, due to the understanding of the micro response and the resin response, this work was able to explain the strain drop that was observed in the prepreg test pre-gelation. The DIC prepreg response was broken down into zones by trends in the behaviour. Creating these zones, it became easier to see the pre- and post-gelation responses and how they compared to the literature. Initially, there is a slight expansion as the material begins to be heated. The average CTE was less than that reported in the literature. After the initial expansion, there is a surface tension dominated region, which can be seen as a large strain drop. At the end of the heating ramp, there is another shift in behaviour after the effects of surface tension have saturated the prepreg. In this zone, there is very little strain response. More work into why this happens is still needed. However, this work speculates the low resin viscosity cases the resin to shear around fibres instead of moving them. The start of the hold marks another zone in which the cure shrinkage response is examined. Results showed that pre-gelation, lowering the temperature, thereby slowing the curing process and increasing the viscosity, leads to a larger strain response to cure in this zone. Post-gelation the strain response to cure is close to that calculated using literature values. Finally, there is the response of the material during the cooling ramp. In this zone, the glassy CTE is captured. The average results were comparable to those reported in the literature.

Tests were done to separate the saturation-induced strain drop from the anticipated thermal expansion pre-gelation by adding an initial hold step. The effect of surface tension was removed by adding a pre-conditioning step, but the prepreg still did not expand thermally as expected. To better understand the differences in response between times where the prepreg responded as predicted and periods that differed the local strain was examined. Local variation in the DIC strain maps suggests non-uniformity of the strain response in regions where the average strain is lagging behind the predicted response.

In addition to comparing local variations to the average transverse strain response, local variations in the strain across the UD prepreg were compared to the morphology of the ply. After comparing the strain and height variations to an SEM image of the ply cross-section, this study predicts the transition from different void densities can be observed through DIC as a transition in the strain response. Additionally, this study found that the size of the peaking in height matches the tow size of AS4/8552. Examination of the surface morphology using IR thermography and optical

microscopy found resin-rich lines evenly spaced 1mm apart across the sample. Future studies with larger sample sizes are needed to support these observations.

6.2 Conclusions

Before this work, very few studies discussed the pre-gelation behaviour of prepreg and even fewer mentioned surface tension as a force that could impact the behaviour of the composite. Although there has been research performed on RTM and other infusion techniques that have looked at the system as a liquid flowing through a porous medium for a long time, when it comes to prepreg, the traditional approach has been to think about the resin pre-gelation as a low modulus solid. When starting with this assumption, it would be reasonable to simplify the system and come up with the free strain model represented by Figure 2.4. However, the work done in this thesis has shown that this assumption is incorrect.

This work conclusively shows that one cannot think of resin in the pre-gelation as a solid but must consider the strong influence of the resins liquid properties. In addition, the interfacial relationships between a solid fibre and a liquid resin and the variability in the material amplifies the need to consider the fluid flow during prepreg processing. Without the consideration of surface tension or the consideration of the temperature dependence of a liquid, all pre-gelation models are flawed. Only when the pre-gelation composite is no longer expected to follow simple solid mechanical rules can a model that truly represents the system be built.

By exploring the development of free strains in prepreg with a particular focus on the pre-gelation regime, several smaller conclusions contributed to the development of this work and helped to develop the conclusion that a solid mechanic approach is inappropriate for this system. These contributions are listed below:

- DIC can be used as a non-contact in situ measurement technique to observe free strains throughout the entire processing cycle for prepreg material.
- Observation and characterization of global and local strain variations on UD prepreg can be made by using DIC.

- The discovery that surface tension consolidation effect is stronger than thermal expansion effect in prepreg processing.
- The observation that the pre-gelation state has an effect on CS and so does temperature.
- The observation that in a liquid state there is a difference between thermal expansion and contraction. Thermal contraction is seen where thermal expansion is not. This is due to the resins tendency to shear under compression.
- Observation of the magnitude of strain variation between 1 and 4 ply samples- effects are present in both, but there are larger variations in strain for 1 ply samples.
- There is a transition between uniform and variant local strains. This transition is linked to the point where the average strain response stops behaving as literature anticipates.
- A novel approach to tracking resin flow into the core of UD prepreg using SEM microscopy. This lead to the visualization of the dominating force capillary driven surface tension has on saturating prepreg.
- Visualization of inconsistencies in ply morphology both in void content and height differences.
- The observation that the morphology of a ply is set initially and, in spite of large deformation, relaxation does not affect the structure thought processing.
- The visualization of resin distribution on the surface of the uncured prepreg.

The contributions of this work will assist in driving forward the understanding of so many different areas of research in composite processing. A better understanding of the capillary driven consolidation can help explain why prepreg loses its tackiness if it is left to sit out for an extended period. Another example, understanding the consolidation forces at play can help improve porosity models that rely on proper timing for prepreg core saturation. This work has explored some of the fundamental behaviours of the composite material, creating a good foundation that can be built upon in the future.

6.3 Future Work

Although this work has uncovered some of the fundamental behaviours prepreg exhibits before gelation, the findings presented in this document have also opened up more questions into the

highly complex pre-gelation region. With these questions comes an opportunity to drive this area of research forward. The following lists some of the potential directions that could be taken;

- AS4/8552 was characterized in this study, performing the same suite of tests on different material systems could uncover the universal trends in the pre-gelation region of all composites.
- The use of DIC as a free strain measurement tool could be implemented on more complex part shapes. Additionally, the relationship between part thickness and observed saturation behaviour could be studied by varying the lay-up of the samples.
- The equipment available during these experiments limited the size of the sample and the processing conditions that could be explored. The creation of a glass oven that could be pressurized would allow for a test that more closely represents manufacturing conditions.
- A simple stress state explanation was presented in this thesis explaining the difference between heating and cooling CTE. To further test this theory molecular modelling of the resins behaviour in compression and tension should be preformed.
- Correlations between strain variations and ply morphology are challenging to make with the small set of data available in this body of work. However, the opportunity to expand this concept and implement it in a digital factory would be an excellent option. Digital factories are built on the idea of using sensors to collect large amounts of data and used machine learning to find relationships that can improve processing. Implementing a measuring step at the beginning of the manufacturing process that would capture the initial condition of the material like the techniques presented in this work, and compare that data with final part quality taken from non-destructive methods, could be an opportunity to make better connections between the initial condition and final quality.

Bibliography

- Kaw AK. 2006.Mechanics of Composite Materials. 2nd ed. CRC Press Taylor & Francis Group; . doi:10.1063/1.1988984.
- Stewart R. 2009."Carbon fibre composites poised for dramatic growth". *Reinf Plast* 2009;53:16–21. doi:10.1016/S0034-3617(09)70148-1.
- Kraus T, Kühnel M, Witten E. 2017. "Composites Market Report 2017". *Carbon Compos* 2017:1–44.
- Fernlund G, Mobuchon C, Zobeiry N. 2017."2.3 Autoclave Processing". *Compr Compos Mater II* 2017;2:42–62. doi:10.1016/b978-0-12-803581-8.09899-4.
- Young W-B. 1996."The Effect of Surface Tension on Tow Impregnation of Unidirectional Fibrous Preform in Resin Transfer Molding". *J Compos Mater* 1996;30:1191–209. doi:10.1177/002199839603001102.
- Anuco S canois. 2000.Permeability and Capillary Pressure Porous in the Infiltration Media of Fibrous in Resin Transfer Moulding. University of Surrey, 2000.
- Francucci G, Vázquez A, Rodríguez ES, Ruiz E. 2010.Capillary Effects in Vacuum Assisted Resin Transfer Molding With Natural Fibers. 10th Int. Conf. Flow Process. Compos. Mater., Monte Verità, Ascona, CH: .
- Yeager M, Hwang WR, Advani SG. 2016."Prediction of capillary pressure for resin flow between fibers". *Compos Sci Technol* 2016;126:130–8. doi:10.1016/j.compscitech.2016.02.014.
- Gangloff JJ, Daniel C, Advani SG. 2014."A model of two-phase resin and void flow during composites processing". *Int J Multiph Flow* 2014;65:51–60. doi:10.1016/j.ijmultiphaseflow.2014.05.015.
- Lawrence JM, Neacsu V, Advani SG. 2009."Modeling the impact of capillary pressure and air entrapment on fiber tow saturation during resin infusion in LCM". *Compos Part A Appl Sci Manuf* 2009;40:1053–64. doi:10.1016/j.compositesa.2009.04.013.
- Vernet N, Ruiz E, Advani S, Alms JB, Aubert M, Barburski M, et al. 2014. "Experimental determination of the permeability of engineering textiles: Benchmark II". *Compos Part A Appl Sci Manuf* 2014;61:172–84. doi:10.1016/j.compositesa.2014.02.010.
- 12. Centea T, Peters G, Hendrie K, Nutt SR. 2017."Effects of thermal gradients on defect formation during the consolidation of partially impregnated prepregs". *J Compos Mater*

2017;51:3987-4003. doi:10.1177/0021998317733317.

- Tucker CLI, Dessenberger RB. 1994. "Governing Equations of Flow and Heat Transfer in Stationary Fiber Beds" 1994.
- Li M, Tucker CL. 2002."Modeling and simulation of two-dimensional consolidation for thermoset matrix composites". *Compos - Part A Appl Sci Manuf* 2002;33:877–92. doi:10.1016/S1359-835X(02)00017-9.
- Tan H, Pillai KM. 2012."Multiscale modeling of unsaturated flow of dual-scale fiber preform in liquid composite molding II: Non-isothermal flows". *Compos Part A Appl Sci Manuf* 2012;43:14–28. doi:10.1016/j.compositesa.2011.06.012.
- Gajo A. 2010."A general approach to isothermal hyperelastic modelling of saturated porous media at finite strains with compressible solid constituents". *Proc R Soc A Math Phys Eng Sci* 2010;466:3061–87. doi:10.1098/rspa.2010.0018.
- Pillai KM. 2002."Governing equations for unsaturated flow through woven fiber mats.
 Part 1. Isothermal flows". *Compos Part A Appl Sci Manuf* 2002;33:1007–19. doi:10.1016/s1359-835x(02)00034-9.
- Rouhi MS, Wysocki M, Larsson R. 2013."Modeling of coupled dual-scale flow– deformation processes in composites manufacturing". *Compos Part A Appl Sci Manuf* 2013;46:108–16. doi:10.1016/J.COMPOSITESA.2012.11.002.
- Mohseni SM, Fernlund G, Lane M. 2018."Cure cycle design to suppress moisture-driven bubble growth in polymer composites". *J Compos Mater* 2018;52:1821–32. doi:10.1177/0021998317734393.
- Stewart AL. 2018.Misalignment defects in unidirectioal composite materails. The University of British Columbia, 2018.
- Stewart AL, Poursartip A. 2018."Characterization of fibre alignment in as-received aerospace grade unidirectional prepreg". *Compos Part A Appl Sci Manuf* 2018;112:239– 49. doi:10.1016/j.compositesa.2018.04.018.
- 22. Wohl C, Palmieri FL, Forghani A, Hickmott C, Bedayat H, Coxon B, et al. 2017."Tack measurements of prepreg tape at variable temperature and humidity". *CAMX 2017 -Compos Adv Mater Expo* 2017;2017-Decem.
- Ahn KJ, Seferis JC, Pelton T, Wilhelm M. 1992."Analysis and characterization of prepreg tack". *Polym Compos* 1992;13:197–206. doi:10.1002/pc.750130308.

- Putnam JW, Seferis* JC, Pelton T, Wilhelm M. 1995."Perceptions of Prepreg Tack for Manufacturability in Relation to Experimental Measures". *Sci Eng Compos Mater* 1995;4:143–54. doi:10.1515/SECM.1995.4.3.143.
- Dubois O, Le Cam JB, Béakou A. 2010. "Experimental analysis of prepreg tack". *Exp* Mech 2010;50:599–606. doi:10.1007/s11340-009-9236-7.
- Garstka T, Ersoy N, Potter KDD, Wisnom MRR. 2007."In situ measurements of throughthe-thickness strains during processing of AS4/8552 composite". *Compos Part A Appl Sci Manuf* 2007;38:2517–26. doi:10.1016/j.compositesa.2007.07.018.
- 27. Schoch KF, Panackal PA, Frank PP. 2004."Real-time measurement of resin shrinkage during cure". *Thermochim Acta* 2004. doi:10.1016/j.tca.2003.12.027.
- Ersoy N, Garstka T, Potter K, Wisnom MR, Porter D, Clegg M, et al. 2010."Development of the properties of a carbon fibre reinforced thermosetting composite through cure". *Compos Part A Appl Sci Manuf* 2010;41:401–9. doi:10.1016/j.compositesa.2009.11.007.
- Hong Y, Mhaisalkar SG, Wong EH. 2005. "Observations of gelation and vitrification of a thermosetting resin during the evolution of polymerization shrinkage". *Macromol Rapid Commun* 2005;26:1483–7. doi:10.1002/marc.200500333.
- Zobeiry N, Vaziri R, Poursartip A. 2018. Autoclave Processing. In: Beaumont PWR, Zweben CH, (eds.), editors. Compr. Compos. Mater. II. 2nd ed., Oxford: Academic Press; , p. 42–62.
- Campbell F. 2004.Chapter 2 Fibers and Reinforcements : The String That Provides the Strength. Manuf. Process. Adv. Compos., Elsevier Ltd; .
- Huang X. 2009. "Fabrication and properties of carbon fibers". *Materials (Basel)* 2009;2:2369–403. doi:10.3390/ma2042369.
- Campbell F. 2004.Manufacturing Processes for Advanced Composites. New York: Elsevier; .
- Wisnom MR, Gigliotti M, Ersoy N, Campbell M, Potter KD. 2006."Mechanisms generating residual stresses and distortion during manufacture of polymer-matrix composite structures". *Compos Part A Appl Sci Manuf* 2006;37:522–9. doi:10.1016/j.compositesa.2005.05.019.
- McCrum NG, Buckley CP, Bucknall B. 1997.Principles of Polymer Engineering. 2nd ed. New York: Oxford University Press Inc.; .

- Flory PJ. 1941."Molecular Size Distribution in Three Dimensional Polymers. I. Gelation". J Am Chem Soc 1941;63:3083–90. doi:10.1021/ja01856a061.
- Ramis X, Cadenato A, Morancho JM, Salla JM. 2003."Curing of a thermosetting powder coating by means of DMTA, TMA and DSC". *Polymer (Guildf)* 2003;44:2067–79. doi:10.1016/S0032-3861(03)00059-4.
- Zobeiry N, Poursartip A. 2015. The origins of residual stress and its evaluation in composite materials. Struct. Integr. Durab. Adv. Compos., p. 43–72. doi:10.1016/B978-0-08-100137-0.00003-1.
- Holst M, Schänzlin K, Wenzel M, Xu J, Lellinger D, Alig I. 2005. "Time-resolved method for the measurement of volume changes during polymerization". *J Polym Sci Part B Polym Phys* 2005;43:2314–25. doi:10.1002/polb.20519.
- Yu H, Mhaisalkar SG, Wong EH. 2005."Cure shrinkage measurement of nonconductive adhesives by means of a thermomechanical analyzer". *J Electron Mater* 2005;34:1177–82. doi:10.1007/s11664-005-0248-5.
- Zobeiry N, Forghani A, Li C, Thorpe R, Vaziri R, Poursartip A, et al. 2016. "Multiscale characterization and representation of composite materials during processing Subject Areas :". *Phil Trans R Soc A* 2016;374:374(2071):20150278. doi:10.1098/rsta.2015.0278.
- 42. Fernlund G, Rahman N, Courdji R, Bresslauer M, Poursartip A, Willden K, et al.
 2002."Experimental and numerical study of the effect of cure cycle, tool surface, geometry, and lay-up on the dimensional fidelity of autoclave-processed composite parts". *Compos Part A Appl Sci Manuf* 2002;33:341–51. doi:10.1016/S1359-835X(01)00123-3.
- Ding A, Li S, Sun J, Wang J, Zu L. 2016."A comparison of process-induced residual stresses and distortions in composite structures with different constitutive laws". *J Reinf Plast Compos* 2016;35:807–23. doi:10.1177/0731684416629764.
- 44. Nawab Y, Casari P, Boyard N, Jacquemin F. 2013."Characterization of the cure shrinkage, reaction kinetics, bulk modulus and thermal conductivity of thermoset resin from a single experiment". *J Mater Sci* 2013;48:2394–403. doi:10.1007/s10853-012-7026-6.
- Zobeiry N, Vaziri R, Poursartip A. 2010."Computationally efficient pseudo-viscoelastic models for evaluation of residual stresses in thermoset polymer composites during cure". *Compos Part A Appl Sci Manuf* 2010;41:247–56. doi:10.1016/j.compositesa.2009.10.009.

- 46. Palardy G. 2007."Resin volumetric changes and surface finish characterization of composite automotive panels By" 2007.
- Garstka T, Ersoy N, Potter KDD, Wisnom MRR. 2007."In situ measurements of throughthe-thickness strains during processing of AS4/8552 composite". *Compos Part A Appl Sci Manuf* 2007;38:2517–26. doi:10.1016/j.compositesa.2007.07.018.
- Svanberg J. M, Holmberg J. A. 2004."Prediction of shape distortions. Part II. Experimental validation and analysis of boundary conditions". *Compos Part A Appl Sci Manuf* 2004;35:723–34. doi:10.1016/j.compositesa.2004.02.006.
- Yeager M, Simacek P, Advani SG. 2017."Role of fiber distribution and air evacuation time on capillary driven flow into fiber tows". *Compos Part A Appl Sci Manuf* 2017;93:144–52. doi:10.1016/j.compositesa.2016.11.016.
- Li M, Wang SK, Gu YZ, Li YX, Potter K, Zhang ZG. 2012. "Evaluation of throughthickness permeability and the capillary effect in vacuum assisted liquid molding process". *Compos Sci Technol* 2012;72:873–8. doi:10.1016/j.compscitech.2012.02.014.
- Li M, Wang S, Gu Y, Zhang Z, Li Y, Potter K. 2010."Dynamic capillary impact on longitudinal micro-flow in vacuum assisted impregnation and the unsaturated permeability of inner fiber tows". *Compos Sci Technol* 2010;70:1628–36. doi:10.1016/j.compscitech.2010.06.004.
- Amini Niaki S. 2017. A three-phase integrated flow-stress framework for process modelling of composite materials. THE UNIVERSITY OF BRITISH COLUMBIA, 2017. doi:https://dx.doi.org/10.14288/1.0355735.
- Ag S, Sector I, Technologies M, Ahmed H, Persson A, Sundqvist L, et al. 2012."Modeling of Transport Phenomena in Porous Media". *Prog Porous Media Res* 2012;02:165–261. doi:10.4236/ns.2010.210132.
- Farnand K, Zobeiry N, Poursartip A, Fernlund G. 2017. "Micro-level mechanisms of fiber waviness and wrinkling during hot drape forming of unidirectional prepreg composites". *Compos Part A Appl Sci Manuf* 2017;103:168–77. doi:10.1016/J.COMPOSITESA.2017.10.008.
- Zobeiry N, Duffner C. 2018. "Measuring the negative pressure during processing of advanced composites". *Compos Struct* 2018;203:11–7. doi:10.1016/j.compstruct.2018.06.123.

- 56. Yuan Y, Lee TR. 2013.Contact Angle and Wetting Properties. doi:10.1007/978-3-642-34243-1.
- 57. de Gennes P-G, Brochard-Wyart F, Quéré D. 2004.Capillarity and Wetting Phenomena. doi:10.1007/978-0-387-21656-0.
- Potter K, Langer C, Hodgkiss B, Lamb S. 2007. "Sources of variability in uncured aerospace grade unidirectional carbon fibre epoxy preimpregnate". *Compos Part A Appl Sci Manuf* 2007;38:905–16. doi:10.1016/j.compositesa.2006.07.010.
- Farhang L. 2014. Void evolution during processing of out-of-autoclave prepreg laminates. University of British Columbia, 2014. doi:10.14288/1.0166064.
- 60. Farhang L, Fernlund G. 2016."Void and porosity characterization of uncured and partially cured prepregs". *J Compos Mater* 2016;50:937–48. doi:10.1177/0021998315583924.
- Khoun L, Hubert P. 2010."Cure shrinkage characterization of an epoxy resin system by two in situ measurement methods". *Polym Compos* 2010;31:1603–10. doi:10.1002/pc.20949.
- Oberholzer TG, Grobler SR, Pameijer CH, Rossouw RJ. 2002."A modified dilatometer for determining volumetric polymerization shrinkage of dental materials". *Meas Sci Technol* 2002;13:78–83. doi:10.1088/0957-0233/13/1/310.
- 63. Nawab Y, Shahid S, Boyard N, Jacquemin F, Nawab Y, Shahid S, et al. 2019."Chemical shrinkage characterization techniques for thermoset resins and associated composites To cite this version : HAL Id : hal-01005857 Chemical shrinkage characterization techniques for thermoset resins and associated composites" 2019.
- Li C, Potter K, Wisnom MR, Stringer G. 2004."In-situ measurement of chemical shrinkage of MY750 epoxy resin by a novel gravimetric method". *Compos Sci Technol* 2004;64:55–64. doi:10.1016/S0266-3538(03)00199-4.
- Ersoy N, Tugutlu M. 2009.Cure Kinetics Modelling and Cure Shrinkage Behaviour of a Thermosetting Composite. ICCM 17.
- Ersoy N, Tugutlu M. 2010. "Cure Kinetics Modeling and Cure Shrinkage Behavior of a Thermosetting Composite". *Polym Eng Sci* 2010;47:21–5. doi:10.1002/pen.
- 67. Takeda N, Okabe Y, Kuwahara J, Kojima S, Ogisu T. 2005."Development of smart composite structures with small-diameter fiber Bragg grating sensors for damage detection: Quantitative evaluation of delamination length in CFRP laminates using Lamb

wave sensing". *Compos Sci Technol* 2005;65:2575–87. doi:10.1016/J.COMPSCITECH.2005.07.014.

- 68. Minakuchi S, Takeda N. 2013."Recent advancement in optical fiber sensing for aerospace composite structures". *Photonic Sensors* 2013;3:345–54. doi:10.1007/s13320-013-0133-4.
- 69. Hudson a. J, Martin SC, Hubert M, Spelt JK. 2002."Optical Measurements of Shrinkage in UV-Cured Adhesives". *J Electron Packag* 2002;124:352. doi:10.1115/1.1498264.
- Mobuchon C, Zobeiry N, Duffner C, Poursartip A. 2018. A Multifaceted Approach for Process Characterization of Polymer- matrix Composites. 12th Canada-Japan Work. Compos., Takayama: , p. 1–8.
- 71. Mobuchon C, Poursartip A. 2019.Linear dependences of the cure shrinkage and thermal expansion of thermoset polymers on degree of cure Christophe. Vancouver: .
- 72. Sharp LJ, Choi IB, Lee TE, Sy A, Suh BI. 2003."Volumetric shrinkage of composites using video-imaging". *J Dent* 2003;31:97–103. doi:10.1016/S0300-5712(03)00005-8.
- Tiba A, Charlton DG, Vandewalle KS, Ragain JC. 2005."Comparison of two videoimaging instruments for measuring volumetric shrinkage of dental resin composites". J Dent 2005;33:757–63. doi:10.1016/j.jdent.2005.02.004.
- 74. Exner W, Kühn A, Szewieczek A, Opitz M, Mahrholz T, Sinapius M, et al.
 2016. "Determination of volumetric shrinkage of thermally cured thermosets using videoimaging". *Polym Test* 2016;49:100–6. doi:10.1016/j.polymertesting.2015.11.014.
- 75. Knowles KR, Tu J, Wiggins JS. 2017."Thermal and volumetric property analysis of polymer networks and composites using elevated temperature digital image correlation". *Polym Test* 2017;58:48–53. doi:10.1016/j.polymertesting.2016.12.013.
- Heinz S, Tu J, Jackson M, Wiggins J. 2016. "Digital image correlation analysis of strain recovery in glassy polymer network isomers". *Polymer (Guildf)* 2016;82:87–92. doi:10.1016/j.polymer.2015.11.026.
- 77. Lyons JS, Liu J, Sutton MA. 1996."High-temperature deformation measurements using digital-image correlation". *Exp Mech* 1996;36:64–70. doi:10.1007/BF02328699.
- Jackson MB, Heinz SR, Wiggins JS. 2012. "Fluid ingress strain analysis of glassy polymer networks using digital image correlation". *Polym Test* 2012;31:1131–9. doi:10.1016/j.polymertesting.2012.08.007.
- 79. HEXCEL. 2016."HexPly® 8552 Product Data Sheet". Hexcel 2016:1–6.

- Chatterjee S. 2014. Thermo-mechanical characterization of 8552 resin and AS4/8552 prepreg.
- Schellart WP. 2011."Rheology and density of glucose syrup and honey: Determining their suitability for usage in analogue and fluid dynamic models of geological processes". J Struct Geol 2011;33:1079–88. doi:10.1016/j.jsg.2011.03.013.
- Kravchenko OG, Kravchenko SG, Casares A, Pipes RB. 2015."Digital image correlation measurement of resin chemical and thermal shrinkage after gelation". *J Mater Sci* 2015;50:5244–52. doi:10.1007/s10853-015-9072-3.
- 83. Van Ee D, Poursartip A. 2009."NCAMP Hexply Material Properties Database for use with COMPRO CCA and Raven". *Natl Cent Adv Mater Perform* 2009:141.
- Convergent Manufacturting. 2017. "RAVEN simulation software" 2017. http://www.convergent.ca/products/raven-simulation-software.
- 85. Hexcel. 2016."HexPly 8552". Prod Data Sheet 2016:1–6.
- 86. Hexcel Composites. 2013.HexTow AS4 Carbon Fibre.
- 87. Schneider CA, Rasband WS, Eliceiri KW. 2012."NIH Image to ImageJ: 25 years of image analysis". *Nat Methods* 2012;9:671.
- 88. Raffer G. 2003."ROTARY RHEOMETER". doi:10.1016/j.(73).
- 89. Rust-Oleum Consumer Brands Canada. 2015.Rust-Oleum White Safety Data Sheet.
- 90. Products Krylon. 2019.KRYLON® Camouflage Paint Black-Safety data sheet.
- 91. Marlett K, Ng Y, Tomblin J. 2011."Hexcel 8552 AS4 Unidirectional Prepreg at 190 gsm
 & 35 % RC Qualification Material Property Data Report". *Niar* 2011.
- Johnston AA. 1997. An Integrated Model Of The Development Of Process-induced Deformation In Autoclave Processing Of Composite Structures. THE UNIVERSITY OF BRITISH COLUMBI, 1997.
- 93. Courteau-Godmaire H. n.d.Ply Void Content Analysis.

Appendices

Appendix A Critical Height of a Puddle

The following section describes a test designed to validate the assumption that surface tension is a driving force that acts upon liquid resin when the viscosity drops low enough to allow flow. The following section describes tests done to determine the critical height of 8552 resin. The experimental results are compared to a calculated critical height base of the laws defining surface tension properties. Tests were designed to show that stress relaxation was not the cause of the in-plane shrinkage seen in the resin DIC tests.

A.1 Theory and Calculations

For a droplet of liquid the capillary length, κ^{-1} , defines the length at which gravitational forces begin to have an effect. The capillary length can be found by balancing the Laplace pressure dominating the surface of the droplet, expressed as,

$$P_L = \gamma / \kappa^{-1} \tag{A.1}$$

The internal force induced by hydrostatic pressure given as,

$$P_H = \rho g \kappa^{-1} \tag{A.2}$$

Balancing the forces the capillary length can be solved for,

$$\kappa^{-1} = \sqrt{\gamma/\rho g}$$
 A.3

For large droplets that have a radius greater than the capillary length a critical height parameter, e, can be found by solving for the equilibrium of the horizontal forces acting on a section of the liquid. Figure A.1 shows the forces acting on a large drop.



Figure A.1 A force diagram depicting a large liquid puddle that is affected by surface tension and hydrostatic pressure. The forces acting on the edge of the puddle are marked. Figure modified from [57]

The surface force added to the hydrostatic pressure integrated over the liquids thickness are balanced and can be expressed by the following equation

$$\frac{1}{2}\rho g e^2 + \gamma s o - (\gamma + \gamma s l) = 0$$
 A.4

Young's law (equation 2.4) states that the forces along the line of contact will balance. Setting equation 2.4 equal to A.4. Results in the following relationship,

$$\gamma(1 - \cos\theta) = \frac{1}{2}\rho g e^2$$
 A.5

Form this equation the thickness, e, of a puddle can be found in terms of the critical length.

$$e = 2 \kappa^{-1} \sin \frac{\theta}{2}$$
 A.6

The thickness of the puddle should have a constant critical height assuming constant material and surface properties. A test to ensure that the shrinkage seen previously in DIC test was caused by surface tension forces not a different force such as stress relaxation was created based on the assumption of a constant height. The test developed varied the initial sample thicknesses thickness

of resin samples and observed the final height after the resin was allowed to flow. If surface tension dominated, samples with initial heights lower that then critical height would shrink in-plane and increase in thickness while samples with larger initial thicknesses would spread in-plane and shrink towards the critical height. If stress relaxation was at play the height would not matter. All the samples would behave in the same way, shrinking inward.

The theoretical critical height was calculated using equation A.6 and the following values.

	Table A.1 Approximate Interface and Resin Properties						
	RESIN SURFACE TENSION γlg [mJ/m ²]	DENSITY OF RESIN ρ [kg/m ³]	CONTACT ANGLE θ [°]				
Value	46.1 ± 2.6 *Measured at 40°C	1301	36.6 ±9.9				
Source	[55]	[79]	Optical microscopy analysis of resin samples				

The values presented in Table A.1 were used to calculate the capillary length and critical height found to be 1.9 mm and 1.2 mm respectfully.

A.2 Methods

Samples of Hexply 8552 neat resin were made in a similar way to the resin samples used for DIC testing. Three different initial thicknesses were examined, 0.5mm, 1mm, or 2.5 mm. It was expected that after heating the resin the samples with initial thicknesses below the critical height would increase in thickness and the sample with a larger initial thickness would shrink, all should shift towards the critical height of 1.2 mm as shown in Figure A.2.



Figure A.2 Samples with varying initial thicknesses above and below the calculated critical height.

Initially the samples are formed so they have a uniform shape and only vary in thickness. To create the samples a ball of resin was made and flattened onto a tool which had been coated with 3 layers of Freekot release agent. The sample was heated quickly on the plate to 80°C. After 5-10 minutes at 80°C an aluminum plate with FEP was placed on top of the resin sample and pressed down using a brick for even pressure distribution. Shims of varying length had been placed between the tool and the top plate to control the thickness (0.5mm, 1mm, or 2.5 mm). The top plate was left on the sample for 5 minutes allowing the material to relax in its new disk shape. After the tool, sample, and top plate were moved to a freezer, quenching the sample. After being cooled, the sample was returned to room temperature and a 6 mm diameter stamp was used to make circular samples.

After samples are formed to the correct specification they were placed in a vacuum chamber with a thick aluminum base. The vacuum chamber with samples was placed in an oven, vacuum was applied to the chamber, and the oven was heated at a rate of 30°C/min to 120°C and held at temperature for 5 hours. A simple heat analysis was used to predict the temperature of the tool/sample when in the oven using RAVEN simulation software. Periodic temperature measurements were taken to ensure the prediction was matching the test. Figure A.3 shows the temperature cycle.



Figure A.3 Predicted oven and tool temperatures with periodic validation measurements.

A.3 Results

After the heating process the final thickness of the samples was measured. The initial and final thicknesses of the samples were reported in Table A.2 along with the calculated change in height. Figure A.4 shows the samples before and after being heated.

SAMPLE	INITIAL THICKNESS	FINAL THICKNESS	CHANGE IN THICKNESS
	[mm]	[mm]	[mm]
А	0.77	.828	0.06
В	1.17	1.157	-0.01
С	2.92	1.254	-1.67

 Table A.2 Critical Height Test Sample Thicknesses Before and After Heating



Figure A.4 Critical height test samples before and after heating.



Figure A.5 Sample Thickness Compared to the Calculated Critical Height

A.4 Discussion

The results from this test show a shift from the initial heights to the critical height. These results support the assertion made in this work that surface tension is the dominating force acting on the liquid resin.

Appendix B Prepreg Ply Void Count Analysis

An unpublished code by Hubert Courteau-Godmaire, a member of CRN [93] was developed for image analyses work performed in this thesis. This code took SEM images that had been stitched together and identified the edge of the ply. After the ply was separated from the background thresh holding was applied to locate the darker regions in the ply that are linked to the physical void spaces. The size of the void spaces and position along the ply were measured and exported on the same reference frame as the DIC strain and height data. The void spaces could then be compared to the other data collected on the sample.

Appendix C Issues with Pre-Gelation TMA Measurements

A TMA is a common measuring device that captures dimensional changes for the throughthickness direction of composite prepreg samples. The majority of tests done using the TMA are on partially cured samples. The free strain response of the material is captured and the cure shrinkage response is captured along with the rubbery and glassy CTEs. There is difficulty extending this measuring technique to the pre-gelation region because of tool part interaction. A probe exerts a slight force to stay in contact with the sample and, by doing so, can change the materials response. In addition it is difficult to prevent bonding between the sample and the probe. Adding release films can assist in reducing the tool part interaction, but any expansion of that material is captured by the TMA and could mask the response of the composite due to the small size of samples.

The following work presents several different set-ups for the TMA that were explored. The hope was to capture the through-thickness free strain response form raw material to cured, however this work found that it was difficult to create a system that did not influence the pre-gelation behaviour. The differences in the test set up are explained as well as the reason they failed. The purpose of this work is to highlight the sensitivity of the prepreg material in the pre-gelation region and offer direction for future work.

C.1 Method

TMA tests were performed on AS4/8552 UD prepreg. The samples were laid up in a 4 ply UD laminate, [0]₄. After laying up the sample a 6mm diameter stamp was used to create 6mm diameter circular samples. These samples were debulked at room temperature for 10 minutes before being sandwiched between substrate materials. Tests were done to pick an acceptable substrate material and Table C.3 discusses the material tested and the outcome. Some of the substrate materials had been pre-cycled to reduce any stress relaxation that could occur during processing.

SUBSTRATE	NOTE
Quartz Glass (2 mm)	Bonding to the substrate to increase apparent free strains in direction 3
FEP (25 µm)	Large initial strain drop due to low Tg 60 °C
Polyimide film (27.9 µm)	Slight bonding to the substrate (High Tg 400 °C)
Polyimide film + Frekote 700nc release agent (~30 μm)	The substrate has to be pre-cycled for the Frekote to set

Table C.3 Summary of Substrates Tested for TMA Tests

Polyimide film with Frekote release agent was selected because the substrate had the smallest variation in thickness through the temperature cycle. However, it did require a pre-cycle to ensure the release agent was set.

Figure C.6 shows a pictorial representation of the TMA probe and sample.



TMA Sample and Probe

Figure C.6 TMA sample set up composed of a quartz glass probe and stage with the prepreg sample sandwiched between pre-cycled polyimide film sheets that have been coated with 3 layers of Freekot release agent.

The TMA reports the change in the length between the probe and the stand. To find the approximate response of the prepreg in this test, the response of the substrate must be removed from the response of the final test with the set up seen in Figure C.6.

A baseline test done on the polyimide film coated with Frekote release agent (PI) was used to separate the response of just the prepreg (P) from the total sample (T).

$$\delta T = 2\delta PI + \delta P \to \delta P = \delta T - 2\delta PI$$
C.7

Given the initial thickness of the total system (h_0) and the thickness of the polyimide film (f_0) , the strain in the prepreg can be calculated.

$$h_o = 2f_p + p_0 \to p_0 = h_o - 2f_p$$
 C.8

The strain in the prepreg can be calculated by taking the change in dimension of the prepreg found in Equation C.7 and dividing it by the calculated initial thickness of the prepreg found using Equation C.8.

$$\epsilon P = \frac{\delta P}{p_o} = \frac{\delta T - 2\delta PI}{h_o - f_p}$$
C.9

Several tests were performed to determine the best method for capturing the through-thickness free strain development using the TMA. In addition to the substrate selection, the size of the substrate was seen to have an effect on the test as well as the force that was applied by the probe onto the sample. If the substrate size were too large, the airflow in the temperature chamber of the TMA would cause the material to flutter and shift causing an increase in noise in the sample. Additionally, the sample would slide when it came in contact with the probe and repeatable measurements were difficult. By increasing the force of the probe, noise in the system was reduced. However, with the addition of a force reduces the confidence that the observed measurements are representing the true material behaviour.

C.2 Results

Two tests were performed using different probe forces, the first applied a 0.01 N force, the TMA cycle information for the pre-cycle test and for the total sample test is reported below.

Pre-Cycle TMA Program:

- 1: Force 0.01 N
- 2: Event state On
- 3: Sampling interval 1.00 s/pt
- 4: Equilibrate at -5.00 °C
- 5: Data storage On
- 6: Measure Length
- 7: Mark end of cycle 0

8: Ramp 3.00 °C/min to 180.00 °C 9: Isothermal for 5.00 min 10: Ramp 3.00 °C/min to -5.00 °C 11: Mark end of cycle 1 12: Ramp 3.00 °C/min to 180.00 °C 13: Isothermal for 120.00 min 14: Ramp 3.00 °C/min to -5.00 °C 15: Mark end of cycle 2 16: Ramp 3.00 °C/min to 180.00 °C 17: Isothermal for 5.00 min 18: Ramp 3.00 °C/min to -5.00 °C 19: Mark end of cycle 3 20: Event state Off

Total Sample TMA Program:

1: Force 0.01 N 2: Event state On 3: Sampling interval 1.00 s/pt 4: Equilibrate at -5.00 °C 5: Data storage On 6: Measure Length 7: Ramp 3.00 °C/min to 180.00 °C 8: Isothermal for 120.00 min 9: Ramp 3.00 °C/min to -5.00 °C 10: Mark end of cycle 0 11: Event state Off

The section of the pre-cycle data that contained the main temperature cycle was synchronized with the start of the Total Sample test. Following the calculations discussed previously the strain for the prepreg alone was found and plotted in Figure C.7.



Figure C.7 Calculated through-thickness strain response reported by TMA with a 0.01 N applied probe force.

The second force test was 0.1 N; this increase in force was done to decrease any slippage between the test sample and the probe. The following lists the TMA programs and shows the calculated prepreg response.



Figure C.8 Calculated through-thickness strain response reported by TMA with a 0.1N applied probe force.

Pre-Cycle TMA Program:

- 1: Force 0.10 N
- 2: Event state On
- 3: Sampling interval 1.00 s/pt
- 4: Equilibrate at -5.00 °C
- 5: Data storage On
- 6: Measure Length
- 7: Ramp 3.00 °C/min to 180.00 °C
- 8: Isothermal for 5.00 min
- 9: Ramp 3.00 °C/min to -5.00 °C
- 10: Mark end of cycle 0
- 11: Ramp 3.00 °C/min to 180.00 °C
- 12: Isothermal for 120.00 min
- 13: Ramp 3.00 °C/min to -5.00 °C
- 14: Mark end of cycle 1
- 15: Ramp 3.00 °C/min to 180.00 °C
- 16: Isothermal for 5.00 min
- 17: Ramp 3.00 °C/min to -5.00 °C
- 18: Mark end of cycle 2
- 19: Event state Off

Total Sample TMA Program:

1: Force 0.10 N 2: Event state On 3: Sampling interval 1.00 s/pt 4: Equilibrate at -5.00 °C 5: Data storage On 6: Measure Length 7: Ramp 3.00 °C/min to 180.00 °C 8: Isothermal for 120.00 min 9: Ramp 3.00 °C/min to -5.00 °C 10: Mark end of cycle 0 11: Event state Off

C.3 Discussion

Similarly to what was shown in DIC transverse strain results, the through-thickness strain response of 4 plys of prepreg shows different zones. The zones occur at approximately the same temperature point as they were captured in the previously discussed DIC tests. The following table describes the trends observed in each zone.

ZONE	APPROXIMATE TEMPERATURE RANGE [°C]	0.01 N FORCE TEST	0.1 N FORCE TEST
1 CTE _{Liquid} [10 ^{-6°} C ⁻¹]	-5 - 35	185	193
2- Strain Drop [%]	40 - 105	-0.54	-6.11
3- CTELiquid [10 ^{-6°} C ⁻¹]	120 - 155	Very little strain response	
4- Cure Shrinkage [%]	180	-1.24	-1.24
5- CTE _{Glassy} [10 ⁻⁶ °C ⁻¹]	1805	46.4	28.9

Table C.4 Summary of TMA Results Broken Down Into Zones

Although there are similarities between DIC and TMA results the TMA tests still need further development. Applying a greater force gave cleaner results. However it could have added a compaction pressure that would drive the prepreg saturation. The jump between a -0.54% and - 6.11% strain drop seen in zone two suggests that the added pressure had such an effect and

therefore is not accurately depicting the response of the material. Additional tests are needed to reduce noise in the test procedure while maintaining accuracy.