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Modeling the pultrusion process to obtain low void fraction composites

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MODELING THE PULTRUSION PROCESS TO OBTAIN LOW VOID FRACTION COMPOSITES

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**Thesis submitted to the
College of Engineering and Mineral Resources
at West Virginia University
for the degree of**

**Master of Science
in
Chemical Engineering**

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Department of Chemical Engineering

**Morgantown, West Virginia
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**Keywords: pultrusion modeling, composites, void prediction,
void measurement**

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ABSTRACT

MODELING THE PULTRUSION PROCESS TO OBTAIN LOW VOID FRACTION COMPOSITES

Adam D. Freed

This work was directed at improving the strength and durability of pultruded composites. Pultruded composites are being used in an increasingly wider range of applications, and, as a result, a higher demand has been placed on the performance capabilities of the various components.

One target area for improving composites is the fraction of voids in the final product. The presence of voids in a composite decreases the Interlaminar Shear Strength, provides a site for the formation of fractures, and increases the susceptibility of the part to outside contaminants.

In this work, the various steps of the pultrusion process are analyzed in order that the fraction of voids can be reduced. The goal is to promote uniform resin flow through the glass fibers, while the part is still in the die; this is because increasing resin flow in the die should result in fewer voids in the final product.

To achieve this objective, an existing pultrusion process was analyzed by modeling fluid mechanics, heat transfer and the chemical reactions involved in this process. From the results obtained, three conclusions could be drawn: 1) While pultruding at relatively low processing speeds, changes in processing speed do not have a significant influence in the final void fraction. 2) Void formation is suppressed by operating at the highest pull speed possible, without the exotherm being outside the end of the die. 3) A moderate variation in the temperature of the die will have a negligible impact on the void fraction of the component.

The void fraction of representative composite samples was measured with optical and scanning electron microscopy, and the results validated the above conclusions.

Dedication

I wish to dedicate this work to my Parents and my wife Holly. I credit my parents for building the foundation that I stand on. I appreciate that they have always supported my academic efforts and decisions.

I also owe much to my wife, for she has supported my efforts when things were going well and when things were hard. Her encouragement allowed me to be more productive and further enjoy this academic experience.

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I appreciate all the help I received from Creative Pultrusions, Inc. I especially thank Jay Toddie and Rick Brown. Jay shared knowledge that he has learned through years of hands on experience. Jay was also very kind to open his home to me after a late-night pultrusion run. Rick operated Creative Pultrusions' Differential Scanning Calorimeter when it was important to analyze resin straight from the production line.

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I greatly appreciate the work that Jim Poston did for me at the National Energy Technology Laboratory of Morgantown, WV. He provided Scanning Electron Microscope

photographs of my composite samples. His generous gift of time and resources allowed for a more in-depth study of the voids in our composite samples.

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NOMENCLATURE

t	time, s
ρ	Bulk density, kg/m ³
T	Temperature, K
C_v	Bulk specific heat, J/kg/K
v_z	Pull speed, m/s
k	Bulk thermal conductivity, W/m/K
V_{fiber}	Fiber volume fraction
H_r	Resin system heat of reaction, J/kg
A_i	Pre-exponential constant, s ⁻¹
E_i	Activation Energy, K
P	Pressure, psi and Pa
κ_x	Permeability, cm ²
Q	Energy from chemical reaction, W/m ³
q_l	Heat flux, W/m ²
v_i	Relative resin velocity
τ	Stress, J/m ³
t_c	Characteristic time, dimensionless

Subscripts

$_1$	Reaction step 1
$_2$	Reaction step 2
$_r$	Property of the resin
$_f$	Property of the fibers
$_c$	Concentration
$_i, j, k$	indices for the x, y, z directions
$_{ss}$	Stainless steel

Superscripts

$^m, ^n$	Reaction order
$*$	Indicates dimensionless distance

Chapter 1

INTRODUCTION

Pultrusion processing is widely used for manufacturing continuous fiber composites. Production of these composites typically utilizes fibers and/or fabrics embedded in a matrix of polymeric compound. The fibers generally are fiberglass, but graphite or aramid can also be used. The resin system mostly consists of polyester, epoxy or vinylester resin, and may contain fillers and materials that improve its ability to withstand the environment. Fillers are generally clay or calcium carbonate; they reduce the product cost, improve processability, and reduce shrinkage of the resin. Fibers and resin are chosen based on the desired properties and cost.

Aside from using different types of fibers and fabrics, the properties of a composite can be varied by the type of fiber arrangement used. The simplest fiber arrangement is to place and pull roving along the length of a part. Roving is made of thousands of individual fibers that are loosely bundled together. The fibers in composites are mostly in this form. Fibers can also be used to make mats and fabric. Mats are not often used for their strength but for surface protection of a composite part. Mats have varying density (thickness) and consist of fibers that are coated with products that increase the resilience of the final product to environmental factors such as water, salt, light, acids and bases. Therefore, mats are mostly applied as the outer most fibers of a pultruded component. The newest arrangement of fibers is in the form of fabrics. Fabrics are used in combination with roving to increase the strength of the product. Fabrics consist of rovings that have been woven or stitched or braided together; the pattern influences overall properties of the glass product. Layers of fabric can be combined and stitched together to form “3-D stitched fabrics”. These offer improved strength and stiffness, and also eliminate

failures caused by delamination of the fibers. However, the 3-D stitched fabrics are more difficult to process.

Continuous fiber composites offer many benefits in properties over conventional structural materials. The pultruded material is lightweight, corrosion resistant, and has high tensile strength. On the other hand, it has a higher cost per pound and is less resistant to shear stress. Overall, the cost per unit performance is competitive for replacing structural materials conventionally made of wood, reinforced concrete, and steel.

The pultrusion process is outlined in Figure 1.1. The fibers, generally in the form of roving and fabric, pass through a guiding system and a bath of resin. The guides vary in complexity and number depending on the shape of the part. The goal of the bath is to coat each glass fiber with resin. In some cases, the guides and bath are combined into one step. Just before the fibers and resin enter the die a radio frequency (RF) preheater can be used to increase the temperature of the resin. Most importantly, a die with a constant cross sectional hole is fitted with strategically placed heaters. Energy from the heaters increases the temperature of the resin so that the initiator(s) will decompose and begin the polymerization reaction. A high degree of polymerization is desired for the thermoset resin, so more than one initiator may be added to the resin system. Each initiator would have a different temperature at which it decomposes. After the first initiator

Figure 1.1: Schematic of the Pultrusion Process [1]

starts the reaction, a second initiator can decompose to increase the rate of reaction and achieve a higher degree of polymerization. When the temperature has almost peaked, a third initiator can decompose to ensure that very little resin monomer remains trapped in the composite. The solid composite then exits the die and begins to cool. Finally, it passes through the pullers and is cut into the desired length.

Applications for pultruded fiberglass are growing in number and acceptability. In 1999, about 260 million pounds of pultruded composites were produced [2]. The most common of these products are ladders, decking, and handles for gardening and sports equipment. Applications for the use of composites are growing with most research and development focusing on structural components [2]. Decking has become an area of significant interest. The Federal Highway Administration-USDOT has determined that almost 40 percent of the nation's bridges have deteriorated to the extent that they must be rehabilitated or replaced [3]. Much of this needed work focuses on the decking system. Replacement of a conventional bridge deck riding surface with fiberglass composite instead of another concrete deck will make the driving surface last about three times as long as the conventional concrete deck [4].

In Transportation Research Record 1118, Dunker et al. reported that if strengthening and rehabilitation methods are not developed or made available for the deteriorated bridges in the near future, a large number of bridges will have to be replaced.

1.1 Proposed Work

Superdeck™ is a pultruded fiber reinforced composite that is useful for replacing deteriorated concrete bridge decking and in the construction of new bridges. At present, it is a framework of 8-inch thick trapezoids and 7-inch thick hexagons that are permanently bonded

Figure 1.2: Superdeck™: Hexagon-Trapezoid combination

together using a urethane adhesive. This design improves many of the basic properties for composites that are considered important for structural design. These key properties are strength and stiffness in tension, compression, flexure and shear [5]. The nature of pultrusion allows the components to be made of any desired length. The materials are typically laid out perpendicular to the riding direction, but in some truss bridge decks, they may be laid parallel. A simple schematic of Superdeck™ is shown in Figure 1.2.

Conventional bridge decking is constructed of 8-inch thick concrete and can have an overlay of 3 inches of asphalt. Superdeck™ is a hollow fiber-reinforced polymer (FRP) with a $\frac{1}{4}$ '' to $\frac{3}{8}$ '' polymeric concrete overlay. Together the FRP and the polymeric concrete form Superdeck™, which weigh a fraction (15 ~ 20%) of the concrete deck with polymeric overlay.

Superdeck™ has been in production for four years and was used to build the Wickwire Run Bridge in Taylor County, WV and the Laurel Lick Bridge in Lewis County, WV and many others in Ohio and Pennsylvania. Physical properties of the Superdeck™ used for the bridges in West Virginia are in the middle column of Table 1.1. The values shown in the first column are typical properties of concrete decking. The third column has the properties of the 2nd generation Superdeck. These are the desired properties. The performance capabilities of the three types of decking are captured with the fracture strength and the stiffness ratio. The fraction strength is defined as the force per area required to break the part. In this case, the force was applied along

Table 1.1: Properties of concrete bridge decking, and current and anticipated Superdeck.

	8" concrete deck w/ 3" asphalt overlay	8" Superdeck w/ 1/4" polymer concrete overlay	2 nd Generation 8" Superdeck w/ 1/4" polymer concrete overlay and 3D- fabrics
Weight (lb/ft ²)	125	26	~20
Fracture Strength in Tension (psi)	4000-5000	40,000	~80,000
Stiffness ratio (lb·in ²)	20×10 ⁸ * 2.4×10 ⁸ **	9×10 ⁸	~10 ×10 ⁸

* Before cracking

** After micro-cracks form

the axial direction of the part. The stiffness ratio is defined as Young's Modulus multiplied by Moment of Inertia. This property characterizes how the part flexes as a force is applied. A larger stiffness ratio correlates to a part that bends less.

The tensile strength, bending strength and stiffness ratios were predicted by work at the Constructed Facilities Center of West Virginia University using micro-mechanical tests and also through the finite element models. The predicted values were verified with laboratory scale tests. Some of this work was conducted by Overby [6] who analyzed Superdeck™ in three stages. First, the FRP components were analyzed using the mechanics of composite beams. Second, the FRP deck module was analyzed using a detailed three-dimensional Finite Element (FE) model. In the third stage, the full composite and non-composite action for actual short-span bridges were analyzed using a simplified FE model. From this and other work, it has been concluded that the current properties of Superdeck™ can be improved by increasing the amount of wet out of individual fibers. Basically, when the current Superdeck™ profile is produced on a large scale, it is

thought that a small fraction of the fibers is never wet with resin. As a result, dry spots and voids are formed. The fibers in a void simply slide against each other when stress is applied, because of no resin bond.

By simulating the temperature, pressure, viscosity, degree of cure, and flow characteristics of the resin within the pultrusion die, it should be possible to improve the fiber wet out while also ensuring an even resin cure profile and maximum pull speed. The simulations used to accomplish this are different from what others have computed, not in the methodology used to create them, but in the specified geometry and the boundary conditions applied.

The operating conditions used for Superdeck™ can be changed to improve the product. The improvements originate from the fact that optimization techniques for the pultrusion process are new. For the most part, the cost of optimizing the production of a new profile is too high; hence, general guidelines are followed for process start-up and then the processing parameters are adjusted so that a product with desired and consistent properties is made. This is a trial and error procedure, but one that has been adopted in the pultrusion industry for thirty years.

1.2 Research Objectives

- Develop a 3-dimensional mathematical model that can accurately predict requirements of temperature and pressure profiles in the composite for maximum cure and void minimization. Also establish the degree of cure, viscosity and flow characteristics of the resin in a pultrusion die of simple geometry.
- Using the new model and Superdeck™ resin system characteristics, determine the benefits of tapering the entrance of the die.

- Conduct pultrusion experiments using the optimized line speed and die heater temperature settings. Measure the temperature profile in the composite as it is being pultruded with a thermocouple that is embedded in the composite.
- Determine the degree of cure of the newly pultruded samples using a Differential Scanning Calorimeter.
- Determine the composite void fraction using microscopy techniques. Measure the reduction of strength as a result of the voids.
- By comparing measured temperature profile, degree of cure and void content, verify the accuracy of all model predictions.

Chapter 2

LITERATURE REVIEW

2.1 Voids

The presence of voids in pultruded parts is virtually inevitable; it is an accepted part of the process by both producers and consumers. From the point of view of performance, the presence of voids means that the “performance per pound of composite” is decreased. “Performance” can refer to any of the following properties: interlaminar shear strength, longitudinal and transverse flexural strength and modulus, longitudinal and transverse tensile strength and modulus, compressive strength and modulus, fatigue resistance and high temperature resistance. In 1978, Judd and Wright [7] conducted an appraisal on how voids affect many of the previously listed composite properties. They concluded that the interlaminar shear strength of a composite decreases about 7 percent for each 1 percent of voids up to a total void content of about 4 percent. At higher void fractions, the interlaminar shear strength becomes increasingly dependent on the voids characteristics. For example, a product with a high concentration of voids in just the mats or just the roving will behave differently than a product with dispersed voids.

The strength of a product can be improved by decreasing the void content. So it is important to know the void fraction of a product in order to know if decreasing the void fraction is a good alternative for increasing the product’s performance. Many different methods exist for measuring void fraction. Some of the common methods [7] are outlined below.

The simplest method is to compare the measured composite density to the density of the theoretical component. The theoretical density is determined from the volume fraction of the glass and the densities of the resin and glass. The density of the composite sample should be measured

using one of the methods recognized by ASTM [8]. ASTM suggests that composites with measured void fractions of less than 1% should have their void fraction verified by other tests or experiments.

A second common method for investigating the void content of composites is by microscopy. In this method, a sample is sectioned, polished and viewed with a microscope. Either optical microscopy or scanning electron microscopy can be used to create the micrographs. The void fraction is determined by visually or digitally measuring the area of voids in a micrograph. The accuracy of this method is limited for two reasons. One reason is that a micrograph represents only a small area within the sample. By obtaining micrographs from many different locations within the sample, this limitation can be partially overcome. The other limitation to micrography is that a two-dimensional measurement is applied to a three-dimensional property. By making repeated measurement for one sample this limitation can also be diminished. But, it is important that some of the measurements be made in planes that are perpendicular to the general fiber direction and parallel to the general fiber direction.

Ultrasonic scanning is the best method of measuring void content when it is not possible to use either of the previously described destructive tests. By scanning the sample, an average value for the attenuation of the ultrasound is determined. The void fraction is determined by correlating the measured attenuation to values measured on samples of known void fraction and similar design. Limitations in ultrasonic scanning arise since the attenuation is also influenced by delaminations and the degree of cure of the resin.

Other methods of measuring void content are useful for verifying the results from primary methods of measuring void content. One such test involves measuring the amount of water absorbed after immersing a sample for an extended period of time. This test is complicated when the water does more than just fill voids in the composite. It can dissolve into the resin, hydrolyze

the polymer and leach components out of the composite. More exotic tests can be used for this measurement, but they are normally less practical and more expensive; the reader is referred to the appraisal [7] mentioned earlier if more information is needed.

2.2 Heat Transfer

Work on the modeling of heat transfer in the pultrusion process began in the late 1970's when Price [9] developed a simulation procedure that could predict the temperature profile within the die. His model was simple, yet led the way for research that is growing today. In the past twenty years, research has led to models that can predict profiles for degree of cure of the resin, temperature of the composite and die, and the required pull force. The work initiated by Price has improved from one-dimensional imaginary shapes, to now, where virtually any shape can be modeled in three-dimensions with the obvious (practiced) constraint of constant cross sectional area. Models vary in other ways also; some have developed their solution scheme using a finite difference approach while others use the finite element approach. The difference being that the finite element method allows more freedom when modeling a complex geometry and can converge on a solution more quickly when considering heat conduction in all three dimensions. Methods of predicting rate of heat generation from the exothermic chemical reaction have also become more sophisticated. Detailed characterization of the resin system using Differential Scanning Calorimetry (DSC) can be used to fit parameters for the models. Table 2.1 summarizes what has been accomplished in the past twenty years.

It is useful to point out the milestones that have been passed. In 1986, Ma [13] presented a heat-transfer model that included axial heat conduction. In 1988, Walsh and Charmchi [15] become the first to consider the layer of resin between the die and the bulk flow of pultruded

Table 2.1: Summary of previous pultrusion process heat transfer models.

Year	Author(s) Reference	Dimensions	Solution Scheme*	Decision Variables +	Axial Heat Conduction	Die Shape **	Experimental Results	Reaction Type***
1979	Price[9]	1		T			N	1
1985	Aylward et al [10]	1	FE	T, α			N	2
1986	Han et al [11]	2	FD	T, α	N	C	N	2
1986	Roy [12]	2				I		1
1986	Ma [13]				Y			
1987	Batch and Macosko [14]	2	FE	T, α ,PF	N	C	N	2
1988	Walsh and Charmchi [15]	2	FD	T, α			N	2
1989	Ng and Manas-Zloczower [16]	2	FD	T, α	N	C	Y	3
1990	Viola and Amsterdam [17]	1	FD		N			2
1992	Hackett and Zhu [18]	2	FE					
1993	Chachad et al [19]	2	FD	T, α	Y	F,C	Y	2
1993	Batch and Macosko [20]	2	FD	T, α	N	F	Y	3
1994	Gorthala et al [21]	2	FD			C		2
1994	Gorthala et al [22]	2	FD	T, α		C	Y	2
1996	Chachad et al [23]	3	FD	T, α	Y	I	N	2
1996	Valliappan et al [24]	3	FD	T, α	N	C	Y	4
1997	Kim et al [25]	3	FE	T, α ,PF	N	C,R	Y	4
1998	Kommu et al [26]	2	FE			F	N	
1999	Mustafa et al [27]	3	FE	T, α ,PF		R	N	4

* Finite Difference/Finite Element

+ T-temperature, α -degree of cure, PF-pulling force

** C-cylindrical, I-irregular, F-flat, R-rectangular

*** (1) 1st order Arrhenius, (2) nth order Arrhenius, (3) Mechanistic(4) nth order Arrhenius with 2 steps

product. They assumed a non-slip boundary condition in which the thin layer of resin had a linear velocity profile. Later, Gorthala et al [22] solved the axial and radial momentum balances on the resin annulus to obtain a more accurate velocity profile. In 1989, Ng and Manas-Zloczower [16] analyzed the effect of fillers on the cure reaction in the pultrusion process. In 1993, Batch and Macosko [20] formulated a model which used physical properties of the composite that were dependent on temperature and degree of cure. Chachad et al [23] used a finite difference approach and solved for profiles which included the die. In previous work, the temperature at the composite/die interface was known as a boundary condition and the die was excluded from the model. Temperature is generally measured using thermocouples, and these can be embedded in the die near the composite/die interface or they can be placed in the fiberglass before entering the die. By placing the thermocouple in the die, a variation in processing conditions can be quickly noticed. When the thermocouple is located in the composite, a detailed history is collected for that one section of the part. Kommu et al [26] followed by Mustafa et al [27] created models for the newer Injection Pultrusion (IP) process. IP has gained in popularity because the resin is injected into the die, which creates fewer emissions and better wet-out of the fibers. The model by Kommu et al is applicable for thin parts while Mustafa et al created a model valid for thick parts.

2.3 Pressure

The pressure that is of interest in this work, is the pressure of the resin while it is in the die and before it gels. Under these conditions, pressure gradients can cause the liquid resin to flow relative to the reinforcement. By increasing the potential for flow, it is speculated that the amount of voids in the final composite will be decreased and the composite's overall performance will be increased.

Much of the research involved with pressure and the production of composites has focused on the resin transfer molding (RTM) process. In RTM, resin must be pressurized so that it will flow into a cavity filled with a fiber preform. High pressures are used to quickly fill the mold so that the resin does not cure prematurely. Many of the principles applied in understanding RTM are useful in analyzing pultrusion. These principles include: 1) considering the fiberglass as a porous solid with a permeability that depends on whether the flow direction is parallel or perpendicular to the fiber direction, 2) improving the performance of a part by varying particular processing conditions, and 3) methods for characterizing the fiberglass and resin.

The process of pultrusion has largely been carried out without attention to resin pressure. As detailed in the Introduction, the step of wetting out the fibers is normally accomplished before the fibers are brought together in the final shape. Attempting to cause the resin to flow after the fibers are accumulated resembles RTM. Therefore, theory reported in the literature for RTM will also be used to help describe phenomena in pultrusion.

In an early publication on fluid flow through fiberglass, Williams et al [28] showed how Darcy's law for one-dimensional flow through a porous medium could be applied to the production of composites. More recently, fluid flow modeling has focused on the differences created by permeability variations within a single part. These variations arise from the fiber orientation. In the simplest case of roving, the permeability inside a bundle can be an order of magnitude smaller than the permeability between bundles. Chang and Houring [29] have moved one step farther by investigating how capillary action affects flow through a bed of fibers.

The motivation for modeling the flow of resin within the die was driven by Dube et al [30] after they experimentally showed the value of Injection Pultrusion (IP). They wanted to show how pultrusion could be accomplished without the use of an open resin bath, but as it turns out, their work is finding an application in decreasing the void content in composites. Kardos et al

spearheaded modeling work for the process of IP at Washington University in St. Louis, MO. The apparent intent of their published research was to aid in the design of die geometry and optimize the operating conditions for a given product.

The driving force causing the flow of a resin through fiberglass is a gradient in pressure. Rules for the conservation of mass can be applied to the system to reveal the three factors that influence the pressure of the resin inside the die: initial resin pressure, chemical changes in the resin, and changes in the cross sectional shape of the die. The initial pressure of the resin is zero unless IP is being used. In the case of IP, resin pressure is increased simply by increasing the pressure at which the resin is supplied. There are three possible chemical changes that affect the resin pressure: expansion as the temperature increases, shrinkage as the resin cures and the amount to which the resin compresses when it is pressurized. The resin can also be mechanically pressurized by adding a tapered section to the die. If the cross sectional area of the die (throughout the tapered section) decreases, the induced flow of resin and its inherently high viscosity will cause the pressure to increase as the resin is forced to flow backward relative to the fibers. Sharma et al [31] measured a pressure rise of 130 psi (900 kPa) from a tapered region having a wedge angle of 8° . The actual magnitude of the pressure rise is dependent on characteristic properties of the resin and fiberglass, but it is good to note that a tapered section can significantly increase the pressure of the resin.

Measuring the resin pressure, while it is in the die, is more costly and more invasive than the methods described earlier for measuring temperature. The same types of measurements can be made, they just require more complicated machining (for installation) and more sophisticated probes. The measuring devices are typically diaphragm transducers and fiber optics, these are described in detail below.

Diaphragm transducers [32] can be permanently mounted in the die. An average sensor is 0.003 inch thick, with about 0.002 inch needed for full displacement at the upper limit of pressure measurement. A series of transducers can be mounted between the die entrance and the expected location of the reaction exotherm in order to get a profile of the resin pressure. After the reaction exotherm, the composite will normally shrink away from the walls of the die, so pressure falls to zero. Complications from using diaphragm transducers arise because they do not last very long compared with the expected life of a die. The length of service is shortened because the material of construction of the diaphragm does not withstand prolonged exposure to the abrasive nature of fiberglass. Also, the decision to not utilize the diaphragm is more complicated than unplugging the instrument, it requires filling in the hole created for the diaphragm.

Currently, researchers at the Composite Materials Research Group (CMRG) of the University of Mississippi, among others, are using fiber optics to measure pressure. A fiber optic sensor is embedded with the glass fibers similar to the method of measuring temperature with a thermocouple. Sharma et al [31] from the CMRG have used a Photonetics 1450 fiber-optic pressure probe. From their measurements, the pressure increases throughout the tapered region, levels off, and falls to zero as the resin cures. This would lead to the conclusion that pressure rise from the thermal expansion of the resin is negligible. But thermal expansion of the resin will still be considerable while working with Superdeck™ because there are many differences between what Sharma et al did and what is looked at here. In this work, the resin system, fabric architecture, and fiber volume fraction are all different from that examined by Sharma et al.

One drawback of using fiber-optic pressure probes is that a single pressure profile measurement costs nearly the same as a diaphragm transducer, which is good for many measurements. However, there are many benefits of using the fiber optics. First, no alterations are required to be made to the die, since the measurement device is embedded within the fibers.

Second, transverse dependencies of the pressure can be detected by varying the initial location of the fiber optic probe. Third, pressure profiles for an entire axial location can be determined with the use of one cable. One other problem, which has not been addressed in the literature, has to do with the size of the probes. The Photonetics 1450 fiber-optic pressure probe is 0.8 mm in diameter. This is 40 – 100 times the size of a normal glass fiber. The pressure measured by a probe of this size could be distorted by forces from fibers being compacted into it.

One last phenomenon that is difficult to include in a model is the pressure created by vaporizing components of the liquid resin. One such component, which is found in large concentration in the resin, is styrene. Some data points for the vapor pressure of styrene are listed below in Table 2.2. These data show that under ideal conditions there will be no problem with styrene vaporizing, since the resin used for Superdeck™ will quickly cure at 120°C. But it is possible that small pockets of styrene could be isolated so that they can not react.

2.4 Approach to be Taken

The proposed heat transfer and fluid flow model will predict variables in all three dimensions for rectangular coordinates using a finite difference approach. Temperature, viscosity, and degree of cure will be predicted. Based on the work of others [20], axial heat conduction will be assumed negligible for the reaction medium. This will provide an accurate prediction of variables of interest, yet will not result in a complicated model. In order that the reaction rate be described accurately, a two step, n^{th} order Arrhenius reaction model will be used. Details for the use of a two step reaction model are given in the section on resin characterization.

Resin flow and pressure will be modeled by solving a modified form of Darcy's law using the results from the heat transfer model. Essentially, the theoretical portion of this research

Table 2.2: Vapor Pressure of Styrene [33]

Temperature (°C)	Vapor Pressure (atm)
20	0.006
121	0.5
146	1.0
174	2.0
193	3.0

follows work conducted by Batch and Macosko [34] at the University of Minnesota. This work differs from what is available in the literature in that different boundary conditions, geometry and resin parameters are studied.

Chapter 3

MODEL THEORY

An important focus of this work is not necessarily the modeling of the pultrusion process with new techniques, but the application of existing techniques to a new geometry and different boundary conditions. As opposed to work done previously, the following work incorporates the actual resin system used in the pultrusion of Superdeck™. The resin system samples were obtained during the manufacturing process to include all proprietary ingredients and proportions.

The following section is divided into three parts, which describe the phenomena of heat transfer, fluid mechanics, and a pressure function. The pressure function will be taken to be a surrogate for the void fraction and will be evaluated to minimize the void fraction. It is a combination of terms that are associated with fluid flow. The terms are calculated using the heat transfer and fluid mechanics models.

In order to determine the pressure of the resin within the die, the temperature and degree of cure of the resin must be known at all points in the die. These properties are calculated using the heat transfer model. The pressure function can then be determined from the resin pressure profile and the resin viscosity. This general solution strategy for solving these three parts is presented in Figure 3.1.

3.1 Heat Transfer

This section on the heat transfer model is divided into two parts. The first section discusses the mathematical model used to describe the phenomenon of heat transfer within the composite, as it is being pultruded. The equations used for describing the temperature and degree

of cure are given. In the second part, a detailed analysis of how the equations are solved using the capabilities of the average personal computer is provided. The assumptions and conditions used in solving the equations in both parts are presented. Reasons for why they apply to this problem are also given.

3.1.1 Model Formulation

The heat-transfer and cure for Superdeck™ in the pultrusion process are modeled using rectilinear coordinates. A simplified cross section of a pultrusion die is shown in

Figure 3.1: Solution Strategy for the Pressure Function

Figure 3.2: Pultrusion Die

Figure 3.2. An Eulerian frame of reference is used with the origin taken at the composite/die interface at the entrance. Starting with the general equations of change [35] for transport phenomena, the problem is quickly simplified. The equation of energy in terms of energy and momentum fluxes in the rectangular Cartesian coordinate system is:

$$\begin{aligned}
 \rho C_v \left(\frac{\partial T}{\partial t} + v_x \frac{\partial T}{\partial x} + v_y \frac{\partial T}{\partial y} + v_z \frac{\partial T}{\partial z} \right) = & - \left[\frac{\partial q_x}{\partial x} + \frac{\partial q_y}{\partial y} + \frac{\partial q_z}{\partial z} \right] \\
 - T \left(\frac{\partial P}{\partial T} \right)_r \left(\frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} + \frac{\partial v_z}{\partial z} \right) - & \left\{ \tau_{xx} \frac{\partial v_x}{\partial x} + \tau_{yy} \frac{\partial v_y}{\partial y} + \tau_{zz} \frac{\partial v_z}{\partial z} \right\} \\
 - \left\{ \tau_{xy} \left(\frac{\partial v_x}{\partial y} + \frac{\partial v_y}{\partial x} \right) + \tau_{yz} \left(\frac{\partial v_y}{\partial z} + \frac{\partial v_z}{\partial y} \right) + \tau_{xz} \left(\frac{\partial v_x}{\partial z} + \frac{\partial v_z}{\partial x} \right) \right\} + Q
 \end{aligned} \quad (3.1)$$

Where ρ , C_v , T , and P are the density, specific heat, temperature and pressure of the composite.

The pulling direction is z and the transverse directions are x and y . v , q , and τ are velocity, heat flux and shear stress. This equation states that the energy in a control volume is balanced by conductive heat, mechanical energy, convection, viscous dissipation, and any source terms that may be present. Since the nature of the pultrusion process is continuous, the transient effects of startup and shutdown are unimportant to this analysis; steady state conditions are analyzed. Eq. 3.2 is the result of applying this condition and three assumptions: plug flow in the z direction (i.e. v_x

$= v_y = 0$), negligible axial heat conduction and negligible secondary effects of heating by friction.

The justification of these conditions and assumptions follow. Eq. 3.1 is reduced to

$$\rho C_v v_z \frac{dT}{dz} = - \left[\frac{dq_x}{dz} + \frac{dq_y}{dy} \right] + Q \quad (3.2)$$

In order to justify the assumption of a flat velocity profile, consider work by Gorthala and coworkers [21]. They determined a more accurate flow profile, which involved solving the momentum balance on the resin to account for an annular region of resin flow. Along the inside of the annular region, the resin velocity is equivalent to v_z , the pultrusion pull speed. At the die surface (outer side of the annular region), the velocity of the resin is zero. This annular region was determined to be up to 0.3-mm thick. In the present research, it is assumed that accounting for this thin annular region will have negligible effects on the final overall cure and temperature profiles. It follows then, that since local motion of the resin is neglected, the secondary effects from viscous dissipation will also be neglected.

Validation of the assumption that heat conduction in the axial direction is negligible can be accomplished through an analysis of the Peclet number of the composite at the die centerline. Batch and Macaskso [20] conducted this analysis and showed that heat conduction in the radial (transverse) direction is much larger than conduction in the axial direction for most of the process. Only at the reaction front does axial heat conduction become significant, this is due to the large changes in temperature from the exothermic reaction. The reaction front represents a short region in the die; therefore axial heat conduction will be neglected for this analysis.

Fourier's law of heat conduction [35] is applied to the energy equation in Eq. 3.2 so that it can be made more useful. The final form becomes:

$$\rho C_v v_z \frac{dT}{dz} = k \frac{d^2 T}{dz^2} + k \frac{d^2 T}{dy^2} + Q \quad (3.3)$$

In this equation, the source-term Q is not constant, and is defined as the volumetric rate of heat generated from the exothermic polymerization reaction. It is a function of the rate of reaction and its functional form is determined experimentally. The rate of heat generation term, Q is evaluated by assuming that the total heat generated from the chemical reaction is proportional to the number of moles of reactant present. It is determined from the rate of reaction measured under isothermal conditions. The final form of the equation used to represent Q is

$$Q = \mathbf{r}_r (1 - V_f) H_R \left[A_1 \exp\left(\frac{-E_1}{RT}\right) + A_2 \exp\left(\frac{-E_2}{RT}\right) \mathbf{a}^m \right] (1 - \mathbf{a})^n \quad (3.4)$$

This expression has three main parts:

$\mathbf{r}_r (1 - V_f) H_R$ is the total heat of reaction per volume of composite material,

$\left[A_1 \exp\left(\frac{-E_1}{RT}\right) + A_2 \exp\left(\frac{-E_2}{RT}\right) \mathbf{a}^m \right]$ is the empirical rate of reaction.

α is the degree of cure measured from Differential Scanning Calorimeter experiments.

$(1 - \alpha)$ then is the effective concentration by which the reaction rate is a function of.

An evaluation of these constants is presented later in Chapter 4, entitled “Resin Characterization.”

A detailed derivation of Eq. 3.4 is presented in Appendix A.

3.1.2 Numerical Approach

Equations 3.3 and 3.4 are combined and solved by a finite difference scheme, using the Alternating Direction Implicit (ADI) technique [36]. The equation is discretized twice; one form is explicit in the ‘x’ direction and the other form is explicit in the ‘y’ direction. This characterizes the ADI method and allows a solution to be found without iterating. The details of the ADI method call for the first order partial derivative to be discretized using the Forward Difference formula

and the second order partial derivatives need to be discretized using the Central Difference formula. To clarify some terminology, the direction that is explicit is discretized in the known level (the last level in which the properties are known) and the direction that is implicit is discretized in the unknown level (the level in which a solution is being solved for). The solution for the ADI method is found by marching forward in the z direction. Discretizing (and rearranging into a non-dimensional form) equations 3.3 and 3.4 explicit in the 'y' direction yields

$$\begin{aligned} \frac{\mathbf{r}C_v v_z}{k} \frac{T_{i,j,k+1} - T_{i,j,k}}{Z\Delta z^*} &= \frac{T_{i+1,j,k+1} - 2T_{i,j,k+1} + T_{i-1,j,k+1}}{X^2(\Delta x^*)^2} + \frac{T_{i,j+1,k} - 2T_{i,j,k} + T_{i,j-1,k}}{Y^2(\Delta y^*)^2} \\ &+ \frac{\mathbf{r}_r H_r (1 - V_f)}{k} \left[A_1 \exp\left(\frac{-E_1}{RT_{i,j,k}}\right) + A_2 \exp\left(\frac{-E_2}{RT_{i,j,k}}\right) \mathbf{a}^m \right] (1 - \mathbf{a})^n \end{aligned}$$

Rearranging the above equation so the unknown level (k+1 terms) and the known level (k terms) are separated yields

$$\begin{aligned} \frac{\mathbf{r}C_v v_z}{Z\Delta z^*} T_{i,j,k+1} - \frac{k}{X^2(\Delta x^*)^2} (T_{i+1,j,k+1} - 2T_{i,j,k+1} + T_{i-1,j,k+1}) &= \\ + \frac{\mathbf{r}C_v v_z}{Z\Delta z^*} T_{i,j,k} - \frac{k}{Y^2(\Delta y^*)^2} (T_{i,j+1,k} - 2T_{i,j,k} + T_{i,j-1,k}) & \\ + \mathbf{r}_r H_r (1 - V_f) \left[A_1 \exp\left(\frac{-E_1}{RT_{i,j,k}}\right) + A_2 \exp\left(\frac{-E_2}{RT_{i,j,k}}\right) \mathbf{a}^m \right] (1 - \mathbf{a})^n & \end{aligned}$$

By arranging the previous equation into the following tridiagonal matrix, the Thomas Algorithm

$$a_i T_{i-1,j,k+1} + b_i T_{i,j,k+1} + c_i T_{i+1,j,k+1} = d_i \quad (3.5)$$

[36] can be used to solve for T at k+1. In this case, the coefficients are

$$a_i = c_i = -\frac{k}{X^2(\Delta x^*)^2}$$

$$b_i = \frac{\mathbf{r}C_v v_z}{Z\Delta z^*} + \frac{2k}{X^2(\Delta x^*)^2}$$

$$d_i = \frac{\mathbf{r}C_v v_z}{Z\Delta z^*} T_{i,j,k} - \frac{k}{Y^2(\Delta y^*)^2} (T_{i,j+1,k} - 2T_{i,j,k} + T_{i,j-1,k})$$

$$+ \mathbf{r}_r H_r (1 - V_f) \left[A_1 \exp\left(\frac{-E_1}{RT_{i,j,k}}\right) + A_2 \exp\left(\frac{-E_2}{RT_{i,j,k}}\right) \mathbf{a}^m \right] (1 - \mathbf{a})^n$$

One step of the solution process is completed; the known level advances one step and the explicit direction and implicit direction switch. Discretizing (and rearranging into a non-dimensional form) equation 3.3 and 3.4 explicit in the 'x' direction yields results similar to that above. Now the tridiagonal matrix takes the following form,

$$a_j T_{i,j-1,k+2} + b_j T_{i,j,k+2} + c_j T_{i,j+1,k+2} = d_j \quad (3.6)$$

and the coefficients are

$$a_j = c_j = -\frac{k}{Y^2(\Delta y^*)^2}$$

$$b_j = \frac{\mathbf{r}C_v v_z}{Z\Delta z^*} + \frac{2k}{Y^2(\Delta y^*)^2}$$

$$d_i = \frac{\mathbf{r}C_v v_z}{Z\Delta z^*} T_{i,j,k+1} - \frac{k}{X^2(\Delta x^*)^2} (T_{i+1,j,k+1} - 2T_{i,j,k+1} + T_{i-1,j,k+1})$$

$$+ \mathbf{r}_r H_r (1 - V_f) \left[A_1 \exp\left(\frac{-E_1}{RT_{i,j,k+1}}\right) + A_2 \exp\left(\frac{-E_2}{RT_{i,j,k+1}}\right) \mathbf{a}^m \right] (1 - \mathbf{a})^n$$

By alternating the direction that is implicit the potential errors are minimized. Solution accuracy is also a function of the step sizes that are used. By choosing a step size that is too large, error will creep into the solution due the linear approximation in the discretization step. On the other hand, a step size that is too small invites error from the truncation of computed values.

Not only should a step size be chosen so that error is minimized but it is also important to minimize the time required to solve the equations.

3.1.3 Model Validation

Preliminary results of the heat transfer model are given in Figure 3.3 for the case when there is no reaction. This is modeled by setting the values for the activation energy of the reaction (E_1 and E_2 in Eq. 3.4) very high, effectively turning off the reaction. This figure also serves to verify the accuracy of the model by comparing the results from the FD model to that of an analytical solution. For the FD model, a flat plate is examined; it has dimensions of 76 mm by 5 mm with an initial temperature of 20 °C and a die temperature of 100 °C. The data in the figure represent the temperature near the center of the die, 38 mm from one wall and 2.5 mm from the other. The same boundary conditions are used with the analytical solution. The profile is measured at 2.5 mm from the wall. In the analytical solution the following equation was solved:

$$\frac{\partial T}{\partial z} = \frac{k}{\rho C_p v_z} \left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} \right) \quad (3.7)$$

The solution to this equation can be found in an advanced heat transfer book [37] and is:

$$\frac{T - T_{die}}{T_{initial} - T_{die}} = \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} \frac{16}{nm\pi^2} \sin[n\pi y] \sin[m\pi x] e^{-[n^2 + m^2]\pi^2 t_c} \quad (3.8)$$

$$\text{where } t_c = \frac{k}{\rho C_p v_z L^2} z, n=1,3,5\dots \text{ and } m=1,3,5\dots$$

In Figure 3.3, there are four series of data. The points represent solutions to Eq. 3.8 and the line are from the proposed model. The three lines show the effect of changing the calculation step size in Eqs. 3.5 and 3.6. The highest line, which most closely represents the analytical

solution, is based on $\Delta x = 0.000625$ and $\Delta y = 0.00125$. The middle curve was calculated with $\Delta x = 0.0025$ and $\Delta y = 0.005$ and for the lower curve), $\Delta x = 0.005$ and $\Delta y = 0.01$. Differences in the curves are small; but as shown by the expanded region in the graph, the model under predicts the analytical solution, even at small step size.

When the same three step sizes were used with normal activation energies (E_1 and E_2), similar errors were predicted. Obviously, it would be best for the error to be zero, but it was good to discover that the presence of the chemical reaction does not magnify error growth.

Inferring from Figure 3.3, the best step size is yet smaller than any of those used to create the above curves. Another important factor limits the usefulness of modeling as step size is further decreased, and that is computational time. Since the model involves calculations in three dimensions, decreasing all step sizes by one-half requires eight times as much computational time. The overall limitation of time therefore became the determining factor of how small step size could be. So for Eqs. 3.5 and 3.6 the number of nodal points used in the x, y, and z directions are $200 \times 100 \times 152400$ with dimensionless Δx , Δy , and Δz as 0.005, 0.01 and 6.5×10^{-6} respectively.

3.2 Fluid Mechanics

Similar to the heat transfer model previously presented, the goal with the fluid flow model is not to improve the techniques used in modeling resin flow, but to apply the existing ones to improve the performance of Superdeck™ by decreasing the void fraction. The general steps in the pultrusion process were described earlier, but now it is beneficial to look at what happens to the composite on a micro level.

Figure 3.3: Verification of model with analytical solution. The filled boxes are from the analytical solution. Lines correspond with solutions from the model, $\Delta x = 0.000625$ and $\Delta y = 0.00125$ (higher curve), $\Delta x = 0.0025$ and $\Delta y = 0.005$ (middle curve), $\Delta x = 0.005$ and $\Delta y = 0.01$ (lower curve).

The fiberglass, in its various forms, is guided from the spools through a bath of resin to the entrance of the die. The resin bath is maintained at ambient temperature so that polymerization of the resin is negligible. The bath for the Even-Leg-Angle utilized pressure to help fill the individual roving and fabric with resin as they passed through small slits in the side of the bath. At the entrance of the die, the fibers have more than the desired volume of resin wetting them but are not completely wet out yet. Excess resin is stripped from the fibers as they enter the rigid die. Achieving 100% wet out is hindered by the complex geometries that the fibers are woven into.

Since no other mechanical forces are applied through the remainder on the die, the following sections focus on how the properties of the resin and glass can be used to affect

pressure. Specifically, attention will be given to properties that characterize how much volume the resin occupies and how easily it flows through between the fibers. The next part of this section is designated to show how the flow of resin can be modeled.

3.2.1 Model Formulation

The voids that remain in a composite after it has cured will negatively impact the composite's performance. Utilizing the pressure that is already being created in the die and knowing where in the die the resin flows most easily can minimize the size and number of voids. For this model, the resin pressure will be assumed to be dependent on two properties of the composite as it is being produced: temperature and degree of cure. These two properties influence mechanisms that are subtle but are documented in the literature[34]. Thermal expansion and shrinkage act on a molecular level to expand or contract the resin in very small proportions. For this process, the thermal expansion is measurable since the temperature during the process changes as much as 150 °C. Shrinkage, as a result of resin cure, acts to decrease the development of resin pressure. The occurrences of these are individually discussed in this section.

Once the resin is in the die and has past the section cooled by the cooling water, it begins to warm up. Energy in the form of heat is conducted from the die into the composite. As the thermal energy increases, the resin and fibers try to expand. The die is operated as an isometric (constant volume) plug flow reactor so instead of expanding, the composite is pressurized. This is an important step in the process. Pressure differences within the composite cause the resin to flow. Large pressure differences are created from resin expanding and contracting at different locations in the die. As a result, the resin moves around and fills some of the remaining voids.

Since within the die there is plug flow, there is no net flow of resin with respect to the fibers. An example pressure profile is shown in Figure 3.4.

Figure 3.4 shows that the pressure reaches a maximum of 1450 psi about 35% through the die, but falls back to zero in a short distance. The actual model predicts that the pressure falls below zero after about 45% through the die. In reality, the pressure does not decrease below atmospheric but the composite shrinks away from the die. It is appropriate to examine the origin of Figure 3.4.

Consider three phenomena that influence the volume filled by a unit of resin: temperature, cure and pressure. These four properties are related by following equation [34]:

Figure 3.4: Pressure and cure throughout entire die

$$\frac{\bar{V}_f - V_o}{1 - V_o} = -\alpha_v (\bar{T} - T_{amb}) + g\bar{\alpha} + k_b P \quad (3.9)$$

where α_v , γ , and κ_b are the thermal expansion coefficient, the shrinkage during polymerization, and the compressibility respectively. α is the conversion of product. V_o and V_f are the initial and final fiber volume fraction. A bar over the variable indicates that it is an average value (for nodes at constant axial distance). In one dimension, nodal values are averaged using the trapezoidal method,

$$\bar{x} = \frac{1}{N-1} \sum_{i=2}^N \frac{x(i) + x(i-1)}{2} \quad (3.10)$$

where x is the generic variable of interest. Since the region of interest is the one before the composite shrinks from the die, the volume of the composite is constant. Assuming the coefficient of thermal expansion for glass is negligible and that its compressibility is negligible, the volume fractions of the glass and resin are constant and the left side of Eq. 3.9 is zero. Solving for the resin pressure as a function of temperature and cure yields,

$$P = \frac{\alpha_v}{k_b} (\bar{T} - T_{amb}) - \frac{g}{k_b} \bar{\alpha} \quad (3.11)$$

Notice that as average temperature increases the pressure increases and as conversion increases the pressure decreases. Referring back to Figure 3.4, the average temperature rises at almost a constant rate throughout the die, the pressure also rises at nearly a constant rate until the reaction starts about 30% through the die. Once the reaction starts, the conversion increases rapidly and the pressure falls to zero. After that, the composite shrinks away from the die and the pressure is constant at atmospheric.

In using this model, it is also assumed that the void fraction is low and that the change in void fraction has a negligible effect on density. Otherwise, the volume and compressibility of the voids would have to be accounted for in Eq. 3.9. As pointed out earlier in Section 3.1.1, the

boundary layer of resin near the inside edge of the die is thin, so the effect of including the shear stress from the no-slip boundary condition is neglected.

Table 3.1 shows the constants that were used in modeling the pressure profile shown in Figure 3.4. The methods for experimentally determining these constants are detailed in the following chapter.

Table 3.1: Constants for the Pressure model

Pull speed	v_z	30.5 cm/min
Fiber glass volume fraction	V_f	0.4653
Coefficient of thermal expansion	α_v	$1 \times 10^{-4} \text{ } ^\circ\text{C}^{-1}$
Shrinkage from resin cure	γ	0.04
Resin compressibility	κ_b	$7 \times 10^{-6} \text{ psi}^{-1}$

3.3 Pressure Function

Darcy's law for fluid flow through a porous media, Eq. 3.12, states that flow is proportional to pressure gradient and inversely proportional to viscosity when the geometry is

$$Q_f = -\frac{\mathbf{k}_z A_{xs}}{\mathbf{h}} \frac{dP}{dz} \quad (3.12)$$

constant. In the previous section, it was shown that as the composite is pultruded it passes through a pressure spike. Relative to the fibers, a small control volume of resin should move as it passes through the pressure spike. When the pressure is increasing, the resin will be displaced in the negative z direction with respect to the fibers and when the pressure is decreasing, the resin will be pushed in the positive z direction. The overall displacement of resin, as a result of the pressure cycle, is minimal.

As the resin is moving back and forth some of the voided regions will become wet-out. It follows then, that by increasing the displacement of the resin, the void fraction of the final product will be decreased. Therefore it is desirable to maximize the dimensionless quantity, Π , which will be called the pressure function and is defined as

$$\Pi = \int_{z=0}^L \frac{\left| \frac{dP}{dz} \right|}{\bar{\boldsymbol{h}}} dz \quad (3.13)$$

Where L is the distance required for the pressure to pass through the maximum and fall back to zero (atmospheric). The average viscosity, $\bar{\boldsymbol{h}}$, is defined by Eq. 3.10.

A thorough analysis of the pultrusion variables that impact the pressure function will allow the final void fraction and product strength properties to be improved. Before any simulation work can be conducted, the constants involved must be determined. The next chapter outlines how the resin was characterized.

Chapter 4

RESIN CHARACTERIZATION

Since this work was conducted to improve the quality of Superdeck™ it is important to closely characterize all variables of the process. This chapter focuses on characterizing the resin and fiberglass involved in the production of the desired part. Some of the information was obtained through particular manufacturers but the majority being required was measured.

From here on out, when referring to resin, unless otherwise noted, it is assumed that the term resin implies the complete resin system used during the actual pultrusion process. The resin therefore includes the pre-polymer, fillers, fire retardant, pigment, catalyst and other proprietary ingredients. The properties of the resin that are important to this work are those that characterize heat transfer, the polymerization reaction, and some fluid dynamics. Some fiberglass properties are necessary also; particularly those associated with heat transfer.

4.1 Rate of Reaction

The heat generation term expressed in Eq. 3.4 consists of many parameters that must be experimentally determined. These parameters characterize how quickly the reaction will proceed at a given temperature and degree of cure and also predict the rate at which heat will evolve. The parameters are determined using a Differential Scanning Calorimeter (DSC). This type of calorimeter measures the heat that flows into or out of a sample as a function of time.

Before diving into the specifics of fitting an empirical reaction rate equation, Figure 4.1 shows a generic mechanism for making a vinyl ester prepolymer. In this reaction, the prepolymer is made from an epoxy and two molecules of acrylic acid. The thermoset is formed by

crosslinking the prepolymer with styrene. Styrene reacts at the double bonds found at the ends of the long chain, and the cured thermoset resin can be characterized as tough and flexible. These properties arise because there is a low number of crosslinking points between prepolymer molecules. The manufacturers of vinyl ester resins can not only change the acid or the epoxy, but also add chemicals like methacrylic hydroquinone and maleic anhydride to improve resin toughness or flexibility.

The DSC used in this work was a Rheometric Scientific DSC Plus with SID 3.10 analysis software owned by Creative Pultrusions. Samples of 8 – 10 mg of resin were placed in sealed sample pans to contain all the volatile gases. Two types of experiments were conducted: isothermal and dynamic scans. A dynamic scan consists of ramping the temperature of the calorimeter at a constant rate to measure the total heat that can be generated from the resin if it is polymerized completely. The scanning rate is chosen after calibrating the instrument to a certain rate. Calibration involves running a scan on a material with a known melting temperature and

latent heat. For this work, Indium and Tin metals were used to calibrate the instrument at 20°C/min.

The isothermal experiments are used to determine the parameters associated with the rate of reaction. In this type of experiment the sample is heated quickly (100°C/min) to a desired temperature and the energy evolved at that temperature is measured. The tests are considered isothermal because the majority of the reaction after the ramping step is at the set temperature. A complete characterization of the resin consists of a dynamic scan and isothermal scans at selected temperatures between the minimum and maximum temperatures that could occur in the die.

Figure 4.2 shows the energy evolved during the isothermal scans. Seven temperatures from 95°C to 150°C were chosen for the scans. The lower end of the range was chosen as the lowest temperature that the reaction will occur within the time frame of interest. The high end of the range was selected as the highest temperature to operate the DSC without allowing too much error to creep into the results. In all of the tests, the sample was held isothermal at 50°C for 1 minute then the temperature was ramped at a rate of 100°C/min to the desired isothermal condition. The temperature was held constant until the exothermic heat of reaction was no longer measurable. As expected the rate at which energy is released is higher for the samples cured at higher temperatures. Likewise, the reaction ends more quickly as the sample is reacted at increasingly higher temperatures. At 150°C, the resin for Superdeck™ will be 95% reacted within about 80 seconds.

To simplify the development of this empirical rate of reaction it is assumed that there is a linear correlation between the amount of heat released by polymerization and the degree to which the sample is cured. Li et al [40] have described how the different reactivity of the many components of the resin determines which components react first. If the rates of reaction varied

Figure 4.2: Results from Isothermal DSC Scans. 150°C(highest), 140°C, 130°C, 120°C, 110°C, 100°C, and 95°C(lowest).

significantly, then the heat of reaction would depend on which molecules were reacting at any given time.

To warrant the use of the above-mentioned assumption, consider how degree of cure is used in this model. For pultrusion, the degree of cure of the resin is zero at the entrance of the die and nearly one at the end of the die. Knowing exactly how the cure gets from zero to one is not useful at this point. It is useful though, to know the amount of heat that has evolved and thus, the amount that still remains. So, for the present modeling efforts, the degree of cure will refer to the potential heat of reaction and not the number of chemical bonds that can be formed.

Before trying to quantify the extent to which a sample has reacted, it is first necessary to know the total amount of energy that is released when the sample is fully reacted; this is called the total Heat of Reaction. For this work, the quantity was measured with a dynamic DSC scan. Figure 4.3 shows the results of a dynamic scan on Superdeck™ resin. Integrating the area under the curve yields the Heat of Reaction to be 200 J/g. The negative values on either side of the peak reflect the energy needed to increase the temperature of the sample (the specific heat).

Using the total Heat of Reaction and the data from the isothermal reactions in Figure 4.2, the isothermal rate of reaction was calculated for the seven different temperatures. To accomplish this, the parameters in Eq. 3.4 were approximated so that the equation could be used to model the isothermal rate of reaction data.

The first step in determining the remaining six constants of the empirical rate of reaction in Eq. 3.4 was to re-plot the data from Figure 4.2 as the rate of cure vs. cure. A sample curve for the isothermal DSC scan at 120°C is given in Figure 4.4. The curve labeled ‘modeled’ was created from the following constant-temperature version of the rate of reaction Eq. 3.4.

$$\frac{d\mathbf{a}}{dt} = \frac{Q}{\mathbf{r}_r(1 - V_f)H_R} = [k_1 + k_2\mathbf{a}^m](1 - \mathbf{a})^n \quad (4.1)$$

For a first round approximation, m and n can be set to unity. After approximating the k_1 and k_2 values for each isothermal DSC scan, m and n can be chosen to further improve the fit between the modeled and measured values. Inversely varying these two exponents (increasing one while decreasing the other) shifts the peak of the curve left or right. After finding optimal values for the k 's and the exponents, the last constants can be determined. From Eqs. 3.4 and 4.1,

$$k_i = A_i \exp\left(\frac{-E_i}{RT}\right) \quad (4.2)$$

Figure 4.3: Dynamic DSC scan. Scanning rate equals 20°C/min.

Figure 4.4: Rate of Cure curve from an isothermal DSC scan at 120°C.

Initial values for the parameters in Eq. 4.2 are found by regressing a line through the k_1 and k_2 values that made the best fit for the isothermal rate curves. By plotting the $\log k_i$ vs. inverse absolute temperature, E_i is the slope and $\log A_i$ is the y-intercept. Running the simulation with the reaction rate constants determined by this method did not yield results that correlated well with the experimental measurements described in the next chapter.

As revealed by preliminary simulations, the reaction constants, fit using the isothermal DSC scans, were causing the reaction to start early (at lower than expected temperature) and proceed too quickly. The measured quickness of the reaction rate is partially caused by imperfect conditions in the DSC. Figure 4.5 shows how the temperature of the sample passes the desired isothermal condition for each experiment. As a result of the temperature exceeding that which is

Figure 4.5: Temperature profiles from the isothermal DSC scans shown in Figure 4.2.

150°C(highest), 140°C, 130°C, 120°C, 110°C, 100°C, and 95°C(lowest).

accounted for in Eq. 4.2, the measured isothermal rate of reaction is actually for a slightly higher temperature.

Another contribution to the error arises during isothermal DSC scans at high temperature. From Figure 4.2, the original calculations for the rate of cure at 150°C are based on a reaction that starts at 130 seconds. Notice in Figure 4.5, that at 130 seconds, the sample temperature is above 140°C. Therefore, the sample is at a temperature high enough to start the reaction for nearly 30 seconds before any measurable reaction occurs. If the reaction starts prematurely, then the final calculated reaction rate is once again higher than it should be.

To further optimize the ability of the model to simulate the experimental results, the reaction rate parameters were adjusted to account for the less than perfect experimental conditions used in the DSC measurements. The original reaction rate constants fit to the experimental data and the reaction rate constants used in the final model are plotted in Figure 4.6. Table 4.1 gives the values of the reaction parameters used in the final model.

Table 4.1: Reaction parameters for Eqs. 4.1 and 4.2.

A_1	E_1	A_2	E_2	m	n
4 s^{-1}	36.32 KJ/mol	4500 s^{-1}	37.4 KJ/mol	0.75	1.5

Figure 4.6: Reaction rate constants fit from experimental data and those used in the model.

4.2 Specific Heat

The specific heat of the resin is also determined using DSC experiments. Specific heat is simply determined by measuring the amount of heat required to increase the temperature of a unit amount of resin by one degree. The information required for this was obtained in the isothermal tests conducted for the reaction rate experiments above.

By specification, the slope of the asymptote in Figure 4.5 is 100°C/min. Near the end of the temperature ramp for each of the curves, the rate of energy added to the sample approaches a constant value. In the cases where the temperature is ramped for the longest amount of time

(isothermal at 140°C and 150°C) there is a short time when the rate of energy added to the sample is steady. These data points are averaged to find the specific heat.

Figure 4.7 shows a specific region of Figure 4.2 just prior to the exotherm; notice the difference in the time scale. During the time interval of 100 – 120 seconds the energy added to the samples for the 140°C and 150°C runs, reaches a nearly constant value of 2.2 W/g. Since it is known that the temperature is increasing at a rate of 100°C/min, the specific heat of the resin is determined to be 1320 J/kg/°C. This is significantly less than the value of 1770 J/kg/°C used by Batch [34], but in his work the resin system contained less clay filler and no bromine powder (both of which have a specific heat of about 1000 J/kg/°C).

The specific heat of the fiberglass was determined from literature values. Unlike the resin system, which has a different composition for each desired component, the composition of fiberglass is consistent. While the amount of sizing (a chemical applied to the fiberglass to improve the bond strength between the glass and resin) can vary, the specific heat and density of different types fiberglass changes little. Kim et al [25] used fiberglass specific heat of 835 J/kg/°C and for fiberglass density they used 2540 kg/m³.

The resin density was determined to be 1161 kg/m³. Using the previous density and specific heat values, the composite specific heat was calculated with the following equation to be 1003 J/kg/°C, where V_f is the fiber volume fraction and is 0.4653.

$$C = \frac{V_f \mathbf{r}_f}{\mathbf{r}} C_f + \frac{(1 - V_f) \mathbf{r}_r}{\mathbf{r}} C_r \quad (4.3)$$

4.3 Viscosity

Resin flow is related to applied force by the resin viscosity. A less viscous fluid will flow more easily than its viscous counterpart. Resin viscosity plays a significant role in the pultrusion

process, specifically in wetting out the fiberglass. If the viscosity of the resin is too high then it is difficult to wet out the fibers in the center of roving and fabrics. On the other hand, a low viscosity resin will flow off the fibers and back out of the die before the curing reaction is initiated. The resin viscosity is dependent on the relative amounts of each component in the resin. Mold release (oil) is specifically added to some resins to decrease the resin viscosity and make it easier to process.

The viscosity of the resin system used in this work was characterized with a Carri-Med CSL 100 viscometer. The CSL 100 was chosen over a RMS 800 because it is simpler to operate, easier to clean up and the results can be interpreted more quickly.

Figure 4.7: DSC experimental data used for determining resin specific heat

To simplify the analysis of the flow of resin, it is assumed to exhibit Newtonian flow behavior. This approximation should hold since strain rates in the die are low. Following closely the work by Kim et. al. from [25], the following model for viscosity was used.

$$\boldsymbol{h} = \boldsymbol{h}_{\infty} \exp\left(\frac{A}{T} + B\boldsymbol{a}\right) \quad (4.4)$$

Where the viscosity is dependent on temperature and degree of cure and is characterized with three constants. The constants are determined through two series of experiments.

Starting with uncured resin, η_{∞} and A are determined through stress sweep experiments at varying temperatures. Using the CSL viscometer, the horizontal shear stress was ramped over a wide range of values and the strain rate required to produce that stress was recorded. Figure 4.8 shows the experimental results for tests at five different temperatures. A line can be regressed through each series of data to give the viscosity of the resin at each temperature. Figure 4.9 shows how a plot of viscosity versus inverse temperature on a semi-logarithmic scale can be used to quantify the values of η_{∞} and A from Eq. 4.4. From this regression, η_{∞} was calculated to be 2.78×10^{-5} Pa·s and A was found to be 3373 K.

With the previous two constants determined, the viscosity of the uncured resin is known as a function of temperature. Ideally, a similar technique would be used to determine the last constant, B. Stress sweeps could be conducted at increasing degrees of cure; viscosity would then be plotted as a function of cure, and B would easily be calculated. Unlike some polymerization reactions, it is very difficult to start and stop the reaction of a thermoset resin. These resins are designed to cure quickly once the reaction is started. Therefore, so as not to damage any of the laboratory equipment, these experiments were not conducted. The literature was reviewed to find what the dependence of viscosity on cure is. Kim et. al. [25] measured the value of B to be 38.0 for a ‘neat’ vinyl ester resin.

Figure 4.8: Stress/Strain experiments used to determine the resin viscosity.

Figure 4.9: Plot of viscosity and temperature to determine η_{∞} and A for the viscosity model.

Figure 4.10 compares the experimental results to predictions by Eq. 4.4. Both experimental and predicted results are at 45°C. Predictions are shown for three degrees of cure: 0.00, 0.01 and 0.05. Higher degree of cure correlates to steeper slope and higher viscosity. These results show that the effect of cure on viscosity is very strong. This is why it is important that the resin does not begin to cure in or near the entrance of the die.

Figure 4.10: Experimental and predicted results of the stress/strain relationship for the resin at 45°C. Predicted values are shown at 0, 1 and 5% cure. Increased cure correlates to increased slope.

4.4 Compressibility

While most applications allow for liquids (and suspensions) to be considered incompressible, compressibility effects cannot be neglected in pultrusion. Here we determine flow potential based on energy stored in the compressed fluid. The apparatus used to determine the

compressibility of the uncured resin was relatively simple. A hydraulic cylinder was filled with resin and then placed in an Instron machine. The Instron machine measures displacement with applied force. The results of two experiments are shown in Figure 4.11. The large displacement with low force at the beginning of Experiment 1 indicates that the cylinder contained some air. In Experiment 2, extra care was taken to remove pockets of air before the valve was replaced on the cylinder. By averaging the slopes from the two experiments it was determined that the resin in this specific cylinder will compress at 2.5×10^{-5} in/lb. Knowing that the piston inside the cylinder was 1" in diameter and that the cylinder held a maximum of 5 in³, the resin compressibility was determined with Eq. 4.4 to be 5.7×10^{-10} Pa⁻¹. This is less than the value of 10×10^{-10} Pa⁻¹

Figure 4.11: Results of compressing resin in a hydraulic cylinder.

determined by Batch [34], but the resin examined in this work had a higher solids content. The solids, in the form of clay or bromine powder, cause the resin to be less compressible.

$$k_b = \frac{\text{Volume Displaced}}{\text{Resin Volume}} \times \frac{1}{\text{Applied Pressure}} \quad (4.5)$$

4.5 Shrinkage and Thermal Expansion

In the absence of mechanical force, resin volume varies as a function of cure and temperature. As the resin cures, the molecular weight of the polymer portion of the resin increases. The chemical bonds that are created from polymerization decrease the free volume [31] of the resin. Thus the polymer density increases and the resin shrinks. For a similar reason, increasing the temperature of the resin causes its density to decrease and therefore it expands. These two properties were measured independently using a small sample of resin. Resin shrinkage was determined by measuring the change in volume by curing the resin. Resin was poured into a vertical piece of pipe, which was capped on the bottom. The pipe and resin were then placed in an oven at 120°C for 1 hr. A low curing temperature was chosen to minimize styrene evaporation and the consequential void formation. Notice from Figure 4.2, the sample would be mostly cured after a few minutes at this temperature. The cured resin shrinks away from the walls of the pipe and is easily removed. The initial resin volume is determined from measurements of the inside dimensions of the pipe. The final resin volume is determined by measuring the outer dimensions of the resin plug. By repeating this experiment and averaging the results the volumetric resin shrinkage, γ , was found to be 0.04. This value is half of that used by Batch [34] in 1989, which reflects the efforts of pultrusion manufacturers to design resin formulations that shrink less as they cure.

Thermal expansion of the resin is defined as a unit change in volume as a function of temperature. The property was measured by heating a cured resin plug (the same one used for determining the shrinkage) from room temperature to 110°C. The resin volume was determined similar to the shrinkage experiment above. The volumetric coefficient of thermal expansion, α_v , was determined to be $1 \times 10^{-4} (\text{°C})^{-1}$. Again, this number seems reasonable since Batch [34] used a value of $5 \times 10^{-5} (\text{°C})^{-1}$.

The thermal expansion coefficient for the fiberglass was found [42] to be $5.0 \times 10^{-6} (\text{°C})^{-1}$. Since this value is nearly one-tenth of that used for the resin, it is assumed that the thermal expansion of fiberglass is negligible. Therefore, the expansion of the fiberglass is not accounted for in the Pressure model.

4.6 Thermal Conductivity

Composite thermal conductivity was averaged from the individual values for the fibers and for the resin. The fiberglass thermal conductivity was found in literature [25] to be 0.76 W/m/K. Resin thermal conductivity was measured using a cell designed by Rajaiah and coworkers for polymer suspensions. The cell was reported on in [43]. Figure 4.12 shows a simplified sketch of the cell. Hot and cold reservoirs were applied at the outer ends of the steel bars to create a steady state temperature profile through the bars and sample. Heat flux through

Figure 4.12: Schematic of thermal conductivity cell.

the bars and sample was determined with the middle part of Eq. 4.6, where k_{ss} is the thermal conductivity of stainless steel and L_1 is the length between the first and second thermocouple. The thermal conductivity of the stainless steel [33] at 50°C was taken as 15.6 W/m/K. Once the heat flux was determined, an apparent thermal conductivity, k_c , from point 1 to point 4 was determined, where L_c is the length from point 1 to point 4.

$$\frac{q}{A} = k_{ss} \frac{(T_1 - T_2)}{L_1} = k_c \frac{(T_1 - T_4)}{L_c} \quad (4.6)$$

Figure 4.13 shows the measured temperature profile across the apparatus for two experiments. The presence of the resin at a dimensionless distance of 0.5 is obvious by the large jump in temperature.

Resistances-in-series theory was used to derive Eq. 4.7, which can be solved for the resin thermal conductivity, k_r .

$$\frac{L_c}{k_c} = \frac{L_1 + L_2}{k_{ss}} + \frac{L_o}{k_r} \quad (4.7)$$

where L_o is the resin sample thickness. For the resin of interest the average thermal conductivity was determined to be 0.223 W/m/K.

The thermal conductivity for heat flow in a composite in the direction perpendicular to the layout of the fibers was calculated using the following equation [25]

$$k = k_r \left[1 - \sqrt{V_f} + \frac{1}{\sqrt{1/V_f} + k_r/k_f - 1} \right] \quad (4.8)$$

With the previously mentioned values for k_r and k_f and V_f as 0.4653 the composite thermal conductivity is 0.36 W/m/K. While this equation seems unnecessarily complicated, it is used because a simple weighted average is not as accurate. By using Eq. 4.9 the calculated composite

$$k = k_r \frac{1}{V_f/k_f + (1-V_f)/k_r} \quad (4.9)$$

thermal conductivity is 0.33 W/m/K. The weighted average under-predicts the actual thermal conductivity of the composite because the increased heat transfer characteristic of the glass allows the resin to transfer more heat than what it would separate.

Figure 4.13: Temperature measurements from the thermal conductivity cell.

Chapter 5

PULTRUSION EXPERIMENTS

Experiments were conducted as part of this work to verify the simulations that are predicted by the heat transfer and fluid flow models. The experiments consisted of pultruding an Equal Leg Angle profile at varying processing conditions. The Equal Leg Angle profile, shown in Figure 5.1, was substituted for the actual Superdeck™ profile because it is less costly to produce. The obvious concern in substituting Equal Leg Angle for Superdeck™ is whether the substitute can represent the actual part adequately. In an attempt to produce an adequate substitute, the Equal Leg Angle incorporates a fiber architecture and resin system nearly the same as that of Superdeck™. The layers of the fiber architecture for the angle are detailed in Figure 5.2 and the composition of the resin system listed in Table 5.1. In using a different part for the experiments and the analysis, it is assumed that an optimization on processing parameters for the simple profile can be extrapolated to the more complex profile.

The profile of Superdeck™ was shown in Figure 1.2. Superdeck™ consists of multiple parallel plates intersecting at 60 and 120 degree angles. The Equal Leg Angle part consists of two parallel plates intersecting at a 90 degree angle. The entrance to the Equal Leg Angle die has a manifold attached to it. This manifold was not included in the length of the die because it has only a top and bottom, no sides. More specifically, there is an extension bolted to the top and bottom plates, but there is nothing in the region of the shims. There is a taper of 0.015 in/in machined into the 3" manifold, which is currently used only to facilitate alignment of the fibers. Two assumptions were made with regards to this manifold: 1) the manifold remains at ambient temperature, and 2) negligible pressure develops in a manifold with undefinable cross-sectional area.

Figure 5.1: Cross section of the die for the Equal Leg Angle component.

—————	3"	Pultex printed veil
.....	6 ½"	NX1010 (1 oz/ft ²)
—————	6"	TH4000 (40oz/yd ²)
.....	39	62-yield roving (3 bands, spaced 6 roving/inch)
—————	5 ¾"	TH4000
—————	5 ½"	TH4000
—————	5 ½"	TH4000
.....	36	62-yield roving (3 bands, spaced 6 roving/inch)
—————	5 ¼"	TH4000
.....	5 ¾"	NX1010

Figure 5.2: Layers of the fiber architecture of the Equal Leg Angle component.

Table 5.1: Composition of a batch of the resin system

Vinyl ester resin	100 lb
Clay	20 lb
Bromine powder	15 lb
Styrene	3 lb
Antimony trioxide	3 lb
Pigment	3 lb
Glass beads	1 lb
Mold release	1 lb
Catalysts	408 g
UV inhibitor	226 g
Total batch weight	148 lb

The impact of processing conditions on void content was partially examined by varying the pull speed of the process. The angle was pulled at three different speeds: 4, 8 and 12 inches per minute. The pull speed for a product is strongly dependent on its geometric complexity. A part with varying thickness, hollow regions or numerous bends will require slower processing speeds to ensure even cure and even fiber distribution. Throughout the pultrusion industry pull speed ranges from a few inches per minute up through many feet per minute. Researchers at the Composite Materials Research Group at the University of Mississippi have experimented with pull speeds approaching 10 feet per minute [44].

While directly increasing the pull speed can decrease the production costs, this work focuses more on decreasing void content, which improves and lengthens the product's service life. This is mentioned as a justification for the use of seemingly low pull speeds.

The pultruded samples were characterized using three methods: temperature was measured during the production process and the cure and void fraction of the final product was measured in the laboratory. Temperature was measured using thermocouples that were guided into the die along with the fiberglass. It is important to know the temperature of at least one general location: the die/composite interface or the composite centerline. Either of the two temperatures can be used as a boundary condition for the heat transfer model. With other parameters from the resin characterization (equation for the rate of reaction, die geometry and the pull speed), this model is used to predict the temperature throughout the composite. The predicted temperatures can then be compared with experimental results. For this work, the interface temperature was not measured and therefore had to be predicted from the set temperatures of the die and the measured centerline temperature profiles. Table 5.2 shows the details of how the die temperature was controlled. Water at ambient temperature was used to cool the entrance of the die to inhibit premature curing and the possibility of fouling the die for that run. The operator controlled water flowrate with a valve. Eight electric heater platens were bolted to the die, two on the top and two on the bottom for each heating zone. The amount of

Table 5.2: Set temperatures for the die.

Temperature Control Device	Control Method	Die Location	Set Temperature
Cooling Water Loop	Mechanical Valve	2"	~20°C
Heater Platens in Zone 1	Thermocouple at 12" w/TIC	6 – 18"	135°C
Heater Platens in Zone 2	Thermocouple at 24" w/TIC	18 – 30"	163°C

energy supplied to the platens was managed by a computer. A thermocouple mounted inside the top die plate, under the center of one of the platens measures the temperature for the heater control loop.

Once the heat transfer model has been verified, the fluid flow model and pressure function can be analyzed for the different scenarios under consideration. The pressure function data can then be correlated with the measured void fraction of the composite specimens.

The temperature profiles measured during the three experiments are shown in Figure 5.3. Three parts of this curve are worthy of explanation. Focusing on the 4"/min data, the temperature of the composite near the beginning of the die, increases slowly as heat is conducted from the die to the composite. Around the middle of the die, the exothermic reaction sends the temperature to a maximum. Through the last third of the die, the composite cools as heat is conducted from the

Figure 5.3: Measured temperature profiles.

composite back to the die. As the part is pulled at higher speeds, the three phenomena stretch toward the end of the die. Increasing the pull speed much beyond 12"/min would cause the exotherm to be located outside the 36" (0.91m) long die. This would cause the product to blister, rendering it useless. The next chapter focuses on the most common problem perceived to affect composites: voids.

Chapter 6

VOID MEASUREMENT

A void is a region in the composite where there is no resin. The voids of interest range in size from about 5 μm (half the diameter of a small strand of fiberglass) to about 100 μm . In samples with high void contents (greater than 5%) the voids can obviously be larger than 100 μm . On the other end of the spectrum, it is recognized that voids can be smaller than 5 μm , but they will normally be at least the size of the interstitial space between three fibers. The interstitial space enclosed by three fibers represents the smallest space in which resin can be trapped from entering. Therefore, the minimum size for voids is partially a function of fiber diameter. For three 10 μm diameter fibers packed together, the interstitial will be approximately 2 μm across.

Measuring the amount of voids in the composite samples was conducted with three methods. Two methods, Optical Microscopy and Scanning Electron Microscopy, were similar in approach and provided a very detailed look at the voids and their shape. It was through microscopy that the actual void fraction was measured. One other technique, which proved inaccurate due to a limited number of samples, was the method of sample densities.

6.1 Density

Composite void fraction is traditionally measured by comparing the composite density to what it theoretically should be. The Annual Book of ASTM Standards [8] describes how to measure void content of reinforced plastics. The test method describes that composites with void content under 1% are of laminate density quality and should have the true void content verified by complementary tests.

By the time that this method was attempted, only one sample for each processing speed remained. All the other samples had been fractured for tests associated with other research. The volume of the fractured samples could not be accurately determined and therefore the fractured samples could not be analyzed by this test method.

For curiosity, the density of the three unfractured samples was determined and compared with the theoretical density. Table 6.1 shows the results.

Table 6.1: Void fraction as determined by the density method.

Sample pull speed (in/min)	Void Fraction (%)
4	1.5 ± 0.9
8	1.8 ± 0.9
12	-2.2 ± 0.9

Basically, the results from the density comparison are that the composite's void content is near zero. Even by including measurement error it is difficult to draw conclusions from these measurements. To more accurately measure void fraction, samples were viewed under an optical microscope.

6.2 Optical Microscope

Using an optical microscope, the details of the surface of the composite could be understood. The microscope used was a KS 400 Axioskop, mounted with a 35 mm MC 100 Camera. 100 and 160 magnification were used with a maximum resolution of about 5 μm . Resolution was limited due to poor contrast between the two phases. The translucent nature of

fiberglass made it nearly impossible to focus on the composite surface if the fibers were anything but perpendicular to the surface.

Sample preparation was limited to mechanical surface treatment. The composite was cut to 3/8" cubes and set in an epoxy mold for the later processes of grinding and polishing. Two stages of sandpaper were used to grind the surface of the sample flat and remove defects from the cutting process. The surface was polished with 0.3 μm Aluminum Silicate micropolish. Early samples were further polished with 0.05 μm Aluminum Silicate micropolish, but no noticeable difference was found from this step so it was omitted to save time.

After placing a prepared sample in the microscope, a series of pictures was taken perpendicular to the layers of fiberglass. A total of 40 pictures were taken of four different samples with a total analysis area of 50 mm^2 . This represents a path 1.3 mm wide across each sample.

The MC 100 camera is not digital, so the film was professionally developed and then scanned to a JPEG or TIF format. Once in a digital format, Scion Image was used to measure the area of voids on each picture. Appendix C shows an example of this process for a picture taken with the optical microscope. The results of this analysis are shown in Figure 6.1.

Void fraction is a three dimensional property of composites, but it is most accurately measured from two dimensional pictures. Under particular circumstances, it was assumed, that the 'area' void fraction measured in a cross section of the composite is representative of the composite's 'volume' void fraction. The area void fraction can be calculated in the three possible orthogonal planes, x-y, x-z and y-z. Referring back to Figure 3.2, the z axis is in the processing direction, the y axis (vertical axis) has the mat and roving layers, and x axis represents width. Since the process is continuous, it is assumed that the void fraction is constant along the z-axis. Along the x-axis, variation in void fraction is also assumed negligible. But in the y direction, void

Figure 6.1: Fraction of voids measured by two micrography techniques.

fraction is not assumed constant because temperature history varies with proximity to the die/composite interface. It is along the y-axis that variation in void fraction is most apparent. The void fraction is expected to vary mostly through the different layers of fiberglass. So, cross sections along the y-axis were assumed to have void fractions representative of the entire composite. Figure 6.2 shows how the pictures are taken across the 3/8" thick sample to include all the layers of roving and mat.

Even though the photographs taken with the optical microscope provide a more detailed look at voids in a composite than the density method could allow, the lack of resolution and contrast prompted the use of a better micrography technique. Scanning Electron Microscopy was pursued as a method to verify the optical microscope measurements and to more completely understand the nature of the voids.

Figure 6.2: SEM picture of a cross section in the y-z plane of a sample pulled at 4"/min.

6.3 SEM

Sample preparation for SEM required the same sanding and polishing steps that were required for the optical samples. Once the samples had been made smooth, they were coated with a conductive material so that charging effects on the sample surface were minimized. The two samples reported on here were coated with carbon. In preliminary tests, gold was used with the same degree of success. With gold or carbon, resolution of less than $0.5\ \mu\text{m}$ was attainable. As noticeable from the SEM pictures in Appendix C, the resolution was more than enough to distinguish all artifacts of interest.

The SEM was fitted with both Polaroid and digital cameras. The digital camera eliminated the step of film development so that Scion Image could immediately be used to measure the area of voids on each picture. A total of 50 pictures were taken of two different samples with a total analysis area of 1.6 mm^2 . Appendix C shows two examples of this process for pictures taken with SEM. The results of this analysis are shown in Figure 6.1. Since sample coating and the SEM pictures were not done “in house” it was difficult to take micrographs of many samples.

On comparing the results from the Scion Image analysis on the pictures from the optical microscope and SEM, it is difficult to conclude whether void fraction is dependent on pull speed or not. A conclusion that can be drawn from the analysis is that the void fraction varies around 0.6 – 0.8% for pull speeds of 4 – 12"/min. The last method of analysis was employed as a way to determine if the fraction of voids is dependent on pull speed.

Considering the three different possible methods used to measure the void fraction, the following can be stated: 1) The density method is the quickest and easiest, but is not accurate for composites with low void content. 2) Void measurements from SEM pictures yield similar results as those from the optical microscope. Therefore, since optical microscopy is the simpler alternative, it can be confidently used for measuring composite void fraction. 3) The void fraction of the Equal Leg Angle parts is around 0.6 – 0.8%, but without more testing, no dependence of void fraction on pull speed can be established.

The last point is further verified by work conducted by Garland[45] on the same Even-Leg-Angle composite as what was used in this work. Garland showed that physical properties of coupon samples from the part were not dependent on pull speed. She conducted bending tests and measured the ultimate bending strength of samples that were unaged and aged. The aged samples were exposed to various temperatures, freeze-thaw cycles, and stresses for 0, 500, 1000,

1500, 2000 and 3000 hours. After all these tests, the properties of the composite were concluded to be consistent for pull speeds varying from 4, 8 and 12 inches per minute.

Chapter 7

EVALUATION of MODEL RESULTS

Heat transfer and fluid flow models were employed to help pultrude Superdeck™ with fewer voids. In previous chapters, the origins of the models were detailed along with methods for characterizing the product. The aim of this chapter is to evaluate how the models facilitate production of a better product. Results from the heat transfer model are presented first, followed by predictions from the pressure model, finishing with a look at how relative void fraction can be predicted for various processing conditions.

7.1 Heat Transfer Model

The heat transfer model shows how the resin reacts at all points in the die. The degree to which the resin has reacted, or the degree of cure, is difficult to measure during the pultrusion of a product. Therefore, the temperature of the part (at some representative location) is measured using a thermocouple embedded within the fiberglass. With a good understanding of the reactivity of the resin under ideal conditions, the measured temperature profile can be correlated to the degree of cure. The heat transfer model is basically the correlation between time, temperature and the degree of cure.

An obvious constraint for modeling a new set of processing conditions is that the degree of cure should approach unity as the product exits the die; this is equivalent to saying that the resin should be almost fully cured before exiting the die. It is also important to keep the maximum resin temperature below 180°C. Above this temperature, the resin begins to decompose, causing the

composite to darken in color and lose the properties that make it superior to other structural building materials.

Modeling the conditions, which were described in the ‘Pultrusion Experiments’ chapter, allows for a final verification of the model before considering new conditions. In Figures 7.1 – 7.3 the results of modeling the Equal Leg Angle at 4, 8 and 12"/min are presented along with the boundary condition used in the model and the experimentally measured temperature profile. Recall that the boundary condition is the temperature at the die/composite interface. This temperature is an input variable to the model.

The temperature interface was estimated by choosing points which made the predictions from the heat transfer model (reported in Figures 7.1 – 7.3) most closely fit the measured data. The estimated boundary conditions for the three pull speeds are very reasonable. In the first part of the die, the temperature of the boundary is higher than that of the bulk composite.

Figure 7.1: Various temperature profiles at 4"/min.

Figure 7.2: Various temperature profiles at 8''/min.

Figure 7.3: Various temperature profiles at 12''/min.

In the middle of the die, the temperature of both boundary and resin are high because of the exothermic heat of reaction. Near the end of the die the boundary is cooler than the bulk composite and heat flows back into the die.

Some basic trends in the reported temperature profiles are noteworthy. The temperature near the entrance of the die is maintained constant by the cooling water loop, this inhibits premature polymerization. Ideally, polymerization does not start until the resin velocity profile is nearly flat (i.e. no resin flows backward relative to the fibers). After passing the cooling loop, the die temperature steadily increases as a result of heat emitted by the first heat platen. The temperature of the composite at the center lags behind the temperature of the composite near the die. This is because the thermal conductivity of the composite is low, making heat transfer a slow process. As a result, temperature can vary significantly from point to point at any given axial location. Figure 7.4 shows that for processing at 8"/min, the temperature ranges from 140 – 165°C at an axial location of $z = 0.54\text{m}$. This figure also shows how the reaction initiates at the edges first and propagates toward the center. Heat is transferred inward from the top and bottom die walls and also from the energy released by the reaction at the edges. The temperature of the remaining uncured resin increased rapidly as it cures, causing the temperature to rise higher than that of the die. This quick part of the reaction is called the exotherm and is visible in Figures 7.1 – 7.3 by the temperature peak. Only a residual amount of reaction occurs after the exotherm, so the temperature decreases as most of the heat in the composite is lost back to the die.

Comparing the measured and modeled temperature profiles, the slower two speeds were more accurately modeled than the fast speed. At 12"/min, the actual reaction proceeds slower than what is predicted by the model. Explanation of the discrepancy is left to experimental error in determining the rate of reaction constants. At increasingly higher pulls speeds, the thermal gradients in the composite increase and the exotherm ends up spiking higher. At these higher

Figure 7.4: Temperature profile at $z = 0.54$ m for run at $8''/\text{min}$.

temperatures, the accuracy of the model decreases since the rate of reaction parameters were measured up to a maximum temperature of 150°C . Attempting to measure the rate of reaction above 150°C induced excess error, because of heat transfer limitations in the DSC. But, looking at the end use of these intermediate results reveals that the calculations around and after the peak of the exotherm are of relatively less significance than the calculations associated with the first part of the die. By the time the composite exotherms, it has already cured enough that it has shrunk away from the die; any voids present will remain froze where they are.

7.2 Pressure and the Motivation for Resin Flow

Resin pressure, during the processing of the Even Leg Angle and Superdeck™ profiles, varies only with temperature and the degree of cure. The resin expands as the temperature increases and then it shrinks with cure. The resin can potentially flow while it is in the die if large pressure gradients exist and resin viscosity is low. In mathematical terms, the amount to which resin can flow is a function of pressure, viscosity, and the distance under which the given conditions exist.

There are numerous ways to quantify this idea of flow motivation. The chosen method is derived from Darcy's law for flow through a porous media, and is outlined in Chapter 3. Shown by the following five graphs are, step by step, the intermediate results needed to calculate the pressure function. The first of this series of graphs depicts the resin pressure throughout the die for the three experimental pull speeds plus one slower and one faster. Here, the pressure rises smoothly for all five pull speeds as the average temperature increases. The slowest pull speed cures at the shortest axial distance into the die, and therefore its pressure falls to zero in the shortest distance. Notice that, even though the 12"/min curve represent a 300% increase in pull speed over the 4"/min curve, the pressure remains positive for only about a 50% increase in distance. The pressure profile does not lengthen linearly with pull speed because the heater platens remain in a fixed location. To gain more understanding of how resin flow might be influenced, pressure gradient throughout the die is shown in Figure 7.6.

The resin pressure gradient at the beginning part of the die is nearly equivalent for each pull speed. Prior to initiation of the curing reaction, the temperature of the resin is increasing at a steady rate and therefore the pressure gradient is constant at a positive value. As curing initiates,

Figure 7.5: Resin pressure a function of axial position in the die.

Figure 7.6: Resin pressure gradient as a function axial position in the die.

the rate of pressure increase falls to zero; at this point the effect of shrinkage by cure is equal to the thermal expansion. As the reaction reaches its exotherm, the pressure falls toward zero and the pressure gradient becomes very negative. In Figure 7.6, the effect of increasing pull speed can be seen to increase the amount of die under which a pressure gradient exists.

The final resin property to contribute to the pressure function calculations is the viscosity. Resin viscosity is an important part of the equation; as the resin cures its viscosity quickly increases, as it becomes one large macromolecule. Figure 7.7 shows how viscosity trends almost directly oppose the pressure trends. As the resin temperature increases the viscosity decreases; as the resin cures, the viscosity increases. Since viscosity covers a much wider scale than pressure, a log scale is used in Figure 7.7.

The integrand in the derived pressure function equation (Eq. 3.13) is the absolute value of the pressure gradient divided by viscosity. In physical terms, the integrand is basically force

Figure 7.7: Resin viscosity as a function axial position in the die.

Figure 7.8: Position dependent flow motivation.

divided by resistance. These results are shown in Figure 7.8. Each curve comprises of two humps. The first (and larger) hump is the result of high pressure gradient and low resin viscosity. The point where the two humps come together is the point in the die pressure reaches a maximum. The second hump is much smaller than the first because resin viscosity is rapidly increasing. For the 12 and 16 inches per minute cases, the second hump is of negligible size and can not be seen in the figure.

A key result from Figure 7.8 lies in the relative size of the humps in each curve. Regardless of pull speed, the relative size of the hump after the pressure maximum is negligible compared with before the pressure maximum. Therefore, if it is desired to influence resin flow within the die, attention should be focused on parameters associated with the beginning of the die.

Figure 7.9: Pressure Function at various pull speeds.

To determine the total pressure function for each pull speed, the curves in Figure 7.8 are integrated with respect to distance. The final results are presented in Figure 7.9 as pressure function versus pull speed. The graph reveals a highly surprising trend. Operating at too slow or too high of pull speed can adversely affect the part by allowing voids to remain trapped in the part. This is, of course, assuming constant temperature setting for the heater platens. The decreasing trend at the highest pull speed is not entirely surprising. For, if the part is pulled too fast, there is not enough time for the part to fully cure before exiting the die. At low pull speeds, the resin enters the die and is rapidly cured; thus decreasing the opportunity for the resin to flow.

The last section of this chapter correlates the experimentally measured void fraction with the Pressure Function and extrapolates what should occur at pull speeds above and below those used in the experiments.

7.3 Relative Void Fraction

From Figure 6.1 it was concluded that the void fraction does not change significantly as pull speed is varied. This trend was partially predicted with the Pressure Function calculations. For the highest speed, 16"/min, the Pressure Function was predicted to be less than that at 12"/min. This intuitively makes sense and correlates to an increased void content. When the pull speed is decreased below 8"/min, the Pressure Function decreases. This means that slowing the production rate to less than 4"/min could increase the final void content.

By further slowing the pull speed, it is also speculated that the temperature of the die becomes difficult to control. With the current temperature control system, Heater 1 will become less effective as the exotherm moves closer to the location of the thermocouple used for the temperature control loop. At speeds slower than 4"/min, the temperature of the composite is more quickly increased and there is less distance between when it enters the die and when curing begins.

These results are, of course, highly dependent on the set temperature of the heater platens. To increase the Pressure Function without changing the pull speed, the set temperatures for the heaters can be optimized so the temperature is increased, plateaus, and then further increased. During the plateau, the temperature of the composite should be still be increasing, but not enough to initiate the curing reaction. As a result, the pressure remains positive longer and there is more time for the resin to flow. In an attempt to verify this, the set temperatures for the two die heaters were switched. Figure 7.10 shows the results of this experiment and the results of modeling it. Case 1 represents the same 8"/min data that has been reported previously. For Case 2, the set temperatures for the die are changed so that more heat transfer occurs near the entrance of the die. The temperature of the first heater was increased

Figure 7.10: Effects of switching the set temperatures for Heater 1 and Heater 2 for 8"/min. With the temperature of the heater platens shown for Case 2.

from 135°C to 163°C and the temperature of the second heater was decreased from 163°C to 135°C. The pull speed for the second case remained at 8"/min.

While it was desired to show that when the average temperature, prior to resin cure, is higher, the Pressure Function is decreased; calculations revealed that there is no significant change in the predicted Pressure Function between these two cases. For Case 1, $\Pi = 3.8 \times 10^6$ and for Case 2, $\Pi = 3.8 \times 10^6$. Surprisingly, experimental work by Garland [45] confirms these results. Garland measured the strength properties of composite samples by bending tests and found that the differences were not statistically significant with changes in the die temperature. Therefore, the pressure function is not only valid for predicting results based on variations in the pull speed, but also variations in the die temperature.

Chapter 8

CONCLUSIONS & RECOMMENDATIONS

Two models have been created to predict physical properties of Superdeck™ while it is being pultruded. The data obtained from the models are used as input for calculating the newly defined Pressure Function. The Pressure Function is used to predict a relative void fraction, which in turn is used to improve the current production process and product properties.

Recommendations are made for changes to the pultrusion process for the Equal Leg Angle part so that a stronger part may be produced with less processing expenses. Recommendations are also made for further development of the models employed in this evaluation.

8.1 Conclusions

From this work, three main conclusions have been drawn. To start with, the optimum die temperature for a composite with a high degree of cure and low void fraction is dependent on pull speed. At low pull speeds, the heaters can be moved toward the exit end of the die to increase the flow field of the uncured resin. At higher pull speeds the resin exotherm must be within the length of the die. Also related to the processing conditions, is the Pressure Function. The Pressure Function is maximized when the composite spends the most time at intermediate temperatures. The temperature of the composite is classified as intermediate when it is warm compared to ambient temperature but cool enough that the resin does not significantly polymerize.

It was discovered that when varying the pull speed with the set point for the die temperature held constant, a maximum occurs in the predicted Pressure Function. For the optimal

case, the uncured resin remains pressurized for the longest time possible, while also maximizing the pull speed. A constant die temperature is maintained by a cooling loop at the entrance and heaters at two fixed axial locations along the die; under these conditions, pull speed has a strong impact on the Pressure Function. By either slowing the process or speeding it up, the resin spends less time at intermediate temperatures where it can best flow.

The advanced development of Superdeck™ will be supported with the help of the given Cure and Fluid Flow simulations. These two models are used to improve fiber wet-out and increase the pull speed. As a result, the strength and stiffness of the product can be increased and simultaneously the production costs can be decreased. These are excellent outcomes, but as the pultrusion industry expands the envelope of possible applications, the necessity for more accurate simulations of the entire process will increase.

8.2 Recommendations

The next step to improving the models will be to relax some of the assumption used in the current formulation. As pultruded parts gain in complexity (thickness), the effects from axial heat conduction will become increasingly important. Therefore, axial heat conduction will need to be included in the development of a new model. Another assumption that limits the use of the current models is constant physical properties. Future work should include the dependence of temperature and degree of cure on thermal conductivity and specific heat.

For the physical process of pultrusion, two tasks should be done. The content of the vapor within the voids should be verified to be styrene using gas chromatography. This would support the theory that was used in developing the Pressure Function.

New processing conditions for the production of the Equal Leg Angle are suggested on a pseudo “trial and error” basis. The current model predicts that the composite needs to spend more time at intermediate temperature. The easiest way to do this is to slow the process down. But slowing the process is not a good route to consider when production costs push to drive up production speeds. Therefore it is suggested that pull speed be set at 8"/min (since this is the current optimum pull speed) and the temperature and location of the heater platens be changed. The temperature of the first heater should be decreased and it should be moved towards the die entrance. The net result should be a temperature profile that increases more rapidly at the entrance but then levels off before increasing again near the second platen.

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Appendix A

Derivation for the Empirical Rate of Reaction Equation

Appendix A

Derivation for the Empirical Rate of Reaction Equation

The energy source term Q in Eq. 4 of the text represents the amount of energy evolved per volume of composite material per time. A simpler equation for Q could be

$$Q = \rho_r (1 - V_f) H_R \frac{d\alpha}{dt} \quad (A1)$$

H_R is the total heat of reaction of the resin. This is measured with DSC using the ramp method. Further information on using the DSC is found in the Resin Characterization section. α is the degree of cure, so the time derivative of the degree of cure becomes the rate of cure or it can be thought of as a rate of reaction. The product of the heat of reaction and the rate of reaction is the rate of heat generation for the resin. By multiplying this quantity by the resin density, ρ_r , the result is per volume of resin instead of mass. The value within the parenthesis is equivalent to the volume fraction of the resin. The right-hand side of Eq. A1 is the rate of heat generation per volume of composite material. The density, fiber volume fraction, and heat of reaction can all be measured, but an empirical relation must be developed for the degree of cure and its time derivative.

Working backwards, after the heat of reaction has been determined, the DSC can be used to find the degree of cure as a function of temperature and time. Isothermal experiments are conducted so that the cure is determined as a function of time only. An example DSC run might go as follows:

1. Heat the sample at 100°C/min to 120°C.
2. Hold the temperature at 120°C and measure the heat evolved until the reaction has terminated.

When a series of these tests have been conducted for different temperatures a pattern will be noticed. At low temperatures (between ambient and about 50°C) there is no noticeable reaction. It is good to point out that the reaction does occur at low temperatures and that resin should be refrigerated when not being used so that it doesn't gel. At moderate temperatures (from about 80°C to 110°C) the reaction becomes measurable but is still slow. At high temperatures (above 130°C) the resin cures very quickly. Reacting the resin at higher temperatures simply allows the resin to cure in less time. At very high temperatures (above 300°C) the resin degrades and is no longer useful for the application of interest.

The heat of reaction from DSC experiments can be measured two ways. As mentioned earlier, H_R is the total heat of reaction generated from a scan. H_R can be defined as

$$H_R = \int_0^{t_f} \left(\frac{dQ}{dt} \right) dt \quad (A2)$$

where (dQ/dt) is the instantaneous rate of heat generated during the dynamic or isothermal scan. t_f is the amount of time required for the reaction to complete during the scan.

By defining cure as the fraction of potential heat evolved at a constant temperature as a result of polymerization the rate of cure and degree of cure can be defined as¹

$$\frac{d\mathbf{a}}{dt} = \frac{1}{H_R} \left(\frac{dQ}{dt} \right) \quad (A3)$$

$$\mathbf{a} = \frac{1}{H_R} \int_0^t \left(\frac{dQ}{dt} \right) dt \quad (A4)$$

Eqs. A3 and A4 and isothermal scanning tests from the DSC are then used to determine the rate of cure for the resin as a function of the degree of cure and temperature.

¹ M. Dusi, W. Lee, P. Ciriscioli and G. Springer, "Cure Kinetics and Viscosity of Fiberite 976 Resin," Journal of Composite Materials 21: 243-261 (March 1987).

For polymerization reactions, the rate of cure da/dt is commonly expressed using the following empirical equation:

$$\frac{da}{dt} = (K_1 + K_2 a^m)(1-a)^n \quad (A5)$$

The expression in the first set of parenthesis can be thought of as the reaction rate constant and the expression in the second set of parenthesis is the reaction activity². The exponents m and n are constants, independent of temperature. K_1 and K_2 are temperature dependent parameters of the following form:

$$K_1 = A_1 \exp(E_1/T) \quad (A6)$$

$$K_2 = A_2 \exp(E_2/T)$$

A_1 and A_2 are the pre-exponential factors, E_1 and E_2 are the activation energies in units of degree Kelvin, and T is the temperature in degree Kelvin. The values for the constants A_1 , A_2 , E_1 , E_2 , m and n are obtained from curve fitting data from the DSC experiments.

Substituting Eqs. A5 and A6 into Eq. A1 yields the final empirical relation for the energy source term Q .

$$Q = r_r(1-V_f)H_R \left[A_1 \exp\left(\frac{E_1}{T}\right) + A_2 \exp\left(\frac{E_2}{T}\right)a^m \right] (1-a)^n \quad (A14)$$

² H. Fogler, Elements of Chemical Reaction Engineering, 2nd Ed., Prentice Hall, NJ 62 (1992).

Appendix B

FORTRAN Program

Appendix B

FORTRAN Program

PROGRAM RESIN

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!      The purpose of this program is to model the temperature, cure, and pressure of the resin
!      in a pultrusion die. The work is based on a journal article by Kim, Han, Jin, and Lee
!      called 'A Model for Thermosetting Composite Pultrusion Process'
!      Published in Journal of Composite Design' in 1997
!      It is also based on a PhD disertation by Batch called Crosslinking Free Radical Kinetics
!      and the Pultrusion Processing of Composites (1985)
!
      DOUBLE PRECISION R,C,v,C0,C1,kt,Rr,Vf,A1,A2,Hr,m,n,E1,E2
      DOUBLE PRECISION dex,dey,dez,T(0:201,0:101,3),Q(3),z
      DOUBLE PRECISION Ay,By,Ax,Bx
      DOUBLE PRECISION Dy1,Dy2,Dy3,Dy4,Dy5,Dy6
      DOUBLE PRECISION Dx1,Dx2,Dx3,Dx4,Dx5,Dx6
      DOUBLE PRECISION E, F, P, S,Dx(1:100),Dy(1:200)
      DOUBLE PRECISION B(1:200,1:100,0:2),det, BB, TT
      DOUBLE PRECISION AvePres, tec, shrink, comp           !Pressure
      DOUBLE PRECISION viscosity(1:100), visA, visB, AveVis  !viscosity
      DOUBLE PRECISION visinf, Pi(1:100), AvePi             !Pi
      DOUBLE PRECISION dPi(1:100), dPdz
      DOUBLE PRECISION Pres(1:100,0:2)
      DOUBLE PRECISION Wre, Hre, Lre !the real lenth
      INTEGER I, J, K, W, H, L, COUNT,PRINTNUM,Wryte,Wrytedat
      INTEGER Lastprintnum, Printstep
!
      OPEN(UNIT=9, FILE='TWire', STATUS='old')
      OPEN(UNIT=14, FILE='TProfile', STATUS='old')
      OPEN(UNIT=13,FILE='PAngle',STATUS='old')
!
      PRINTNUM = 80001
      Lastprintnum = 140002
      Printstep = 10000
! PRINTNUM should be odd, otherwise, as indicated in the "Do 90" statement there will not be
! any intermediate profiles printed.
      Wryte = 0 ! This is a counting integer used with Wrytedat
      Wrytedat = 20 ! This integer controls how often data is printed for the tracer at about
                   ! line 340 and for the Pi print command before the Dx calcs
!
      R=1800.0           !Calculated from values from Jay Toddie
      C=1003.0           !Vf=.4653, Cr=1320, Rr=1161, Cf=2540, Rf=835
      v=0.00508          ! 12.0 in per min, medium
      kt=0.36            !From Original paper w/ my values for vf & kr=.223
      Rr=1161.0

```

```

Vf = 0.4653      !Jay Toddie
A2=4500.0
A1=4.0
Hr=2.00e5        !From experiments at CP
m=0.75
n=1.5
E1=-4369.0
E2=-4500.0
!
tec = 0.00004
shrink = 0.04
comp = 0.00000000057 ! inverse pascal
!
visA = 3733.0 !Kelvin
visB = 20.0
visinf = 0.00000278 !Pa*sec
!
BB= 0.0
!
W = 200
Wre = 76.0      !mm
dex = 1/200.0
H = 100
Hre = 9.5       !mm
dey = 1/100.0
L = 152400 !at dez=0.006 total l is 36 in
Lre = 914.4     !mm
dez = 1/152400.0
!
! While the lenthls are inputted in millimeters the rest of the program uses them in units of
! meters. Therefore they are converted.
!
Wre = Wre/1000.0
Hre = Hre/1000.0
Lre = Lre/1000.0
det = Lre*dez/v !used in the degree of cure calculations
!
Ay = -kt/dex/dex/Wre/Wre
By = R*C*v/dez/Lre-2.0*Ay
Ax = -kt/dey/dey/Hre/Hre
Bx = R*C*v/dez/Lre-2.0*Ax
!
! Boundary temperatures along the die are modeled by the following functions. T in Celsius
! and z in meters.
!
DO 15 I = 1,W
DO 10 J = 1,H
T(I,J,1) = 21.7 !If change this #, change ambient T in Pres Eq

```



```

10  CONTINUE
15  CONTINUE
!
  DO 90 COUNT = 1,L,2
    Wryte = Wryte + 1
    DO 40 K = 1,3
      z = dez * REAL(COUNT+K-2) !Dimensionless distance
!
!   The following is the temperature at the die/composite interface listed in
!   the journal mentioned above. In their experiments the die had heaters at
!   one location and the temperature was set to 160 degrees Celsius (320 F).
!   This die is 0.6 meters (23 inches) long.
!
    IF (z.LE.0.055) THEN
      P = 37.0
      S = 43.0
      E = 0.0
      F = 0.055
    ELSEIF (z.GT.0.055.AND.z.LE.0.115) THEN
      P = 43.0
      S = 64.0
      E = 0.055
      F = 0.115
    ELSEIF (z.GT.0.115.AND.z.LE.0.164) THEN
      P = 64.0
      S = 80.0
      E = 0.115
      F = 0.164
    ELSEIF (z.GT.0.164.AND.z.LE.0.23) THEN
      P = 80.0
      S = 101.0
      E = 0.164
      F = 0.23
    ELSEIF (z.GT.0.23.AND.z.LE.0.291) THEN
      P = 101.0
      S = 118.0
      E = 0.23
      F = 0.291
    ELSEIF (z.GT.0.291.AND.z.LE.0.325) THEN
      P = 118.0
      S = 127.0
      E = 0.291
      F = 0.325
    ELSEIF (z.GT.0.325.AND.z.LE.0.359) THEN
      P = 127.0
      S = 134.0
      E = 0.325
      F = 0.359

```

```

ELSEIF (z.GT.0.359.AND.z.LE.0.394) THEN
  P = 134.0
  S = 140.0
  E = 0.359
  F = 0.394
ELSEIF (z.GT.0.394.AND.z.LE.0.443) THEN
  P = 140.0
  S = 148.0
  E = 0.394
  F = 0.443
ELSEIF (z.GT.0.443.AND.z.LE.0.492) THEN
  P = 148.0
  S = 156.0
  E = 0.443
  F = 0.492
ELSEIF (z.GT.0.492.AND.z.LE.0.547) THEN
  P = 156.0
  S = 162.0
  E = 0.492
  F = 0.547
ELSEIF (z.GT.0.547.AND.z.LE.0.656) THEN
  P = 162.0
  S = 164.0
  E = 0.547
  F = 0.656
ELSEIF (z.GT.0.656.AND.z.LE.0.766) THEN
  P = 164.0
  S = 167.0
  E = 0.656
  F = 0.766
ELSEIF (z.GT.0.766.AND.z.LE.0.875) THEN
  P = 167.0
  S = 170.0
  E = 0.766
  F = 0.875
ELSEIF (z.GT.0.875.AND.z.LE.1.0) THEN
  P = 170.0
  S = 170.0
  E = 0.875
  F = 1.0
ENDIF
!
Q(K) = S - (S-P)*(F-z)/(F-E)
!
DO 30 J = 0,H+1
  T(0,J,K) = Q(K) !* 1.05
  T(W+1,J,K) = Q(K) !* 1.05
30 CONTINUE

```

```

DO 35 I = 1,W
  T(I,0,K) = Q(K) !* 1.05
  T(I,H+1,K) = Q(K) !* 1.05
35  CONTINUE
40  CONTINUE
!
!   Following, is the calculations for the coefficients of the tridiagonal matrix. C is known to !
!   be equal to A, so A is used in its place. A, B, and C are constants in the matrix. The
!   subscript y is used when the y direction is explicit. The same for x.
!
K = 1
DO 55 J=1,H
  DO 51 I=1,W
    TT = T(I,J,K)
    BB = B(I,J,K-1)
    CALL ITdC(TT,BB,det,A1,E1,A2,E2)
    B(I,J,K) =BB
49      Dy1=R*C/det*(T(I,J,K)+273.15)
          Dy2=-Ax*(T(I,J+1,K)-2.0*T(I,J,K)+T(I,J-1,K))
          Dy3=Rr*(1.0-Vf)*Hr
          Dy4 = A1*DEXP(E1/(T(I,J,K)+273.15))
          Dy5 = A2*DEXP(E2/(T(I,J,K)+273.15))
          Dy6 = B(I,J,K)
          Dy(I)=Dy1+Dy2+(Dy3*(1.0-Dy6)**n*(Dy4+Dy5*Dy6**m))
51  CONTINUE
!   This correction to the initial Dy fixes the falling end problem
      Dy(1) = Dy(1) - Ay * (T(0,J,K+1) + 273.15)
      CALL TRIDAGY(W, Ay, By, Dy, T, J)
55  CONTINUE
!
K = 2
z = dez * REAL(COUNT)
DO 65 I = 1,W
  DO 60 J = 1,H
    TT = T(I,J,K)
    BB = B(I,J,K-1)
    CALL ITdC(TT,BB,det,A1,E1,A2,E2)
    B(I,J,K) =BB
    Dx1 = R*C/det*(T(I,J,K)+273.15)
    Dx2 = -Ay*(T(I+1,J,K)-2.0*T(I,J,K)+T(I-1,J,K))
    Dx3 = Rr*(1.0-Vf)*Hr
    Dx4 = A1*DEXP(E1/(T(I,J,K)+273.15))
    Dx5 = A2*DEXP(E2/(T(I,J,K)+273.15))
    Dx6 = B(I,J,K)
    Dx(J)=Dx1+Dx2+(Dx3*(1.0-Dx6)**n*(Dx4+Dx5*Dx6**m))
!
IF(I.EQ.100) THEN
Pres(J,0) = tec*(T(I,J,K)-21.7)/comp - shrink*B(I,J,K)/comp

```

```

    AvePres = AvePres + Pres(J,0)
    If(J.EQ.1.OR.J.EQ.H) AvePres = AvePres - 0.5*Pres(J,0)
    dPdZ = dPdZ + (Pres(J,0)-Pres(J,2))/(2.0*dez*2.0)
    !one 2 for eq, other 2 because calc is every other t step
    viscosity(J)=visinf*exp(visA/(T(I,J,K)+273.15)+visB*B(I,J,K))
    AveVis = AveVis + viscosity(J)
    If(J.EQ.1.OR.J.EQ.H) AveVis = AveVis - 0.5*viscosity(J)
    ENDIF
60    CONTINUE
!   These corrections to the initial and final Dx's should fix the problem of the ends falling off.
        Dx(1) = Dx(1) - Ax*(T(I,0,K+1)+273.15)
        CALL TRIDAGX(H, Ax, Bx, Dx, T, I)
65    CONTINUE
!
        AvePres = AvePres/(Real(H)-1.0)
        dPdZ = dPdZ/(Real(H)-1.0)
        AveVis = AveVis/(Real(H)-1.0)
!
        DO 68 J=1,H
!           dPi(J)=abs(dPdZ)/viscosity(J)*dez*2.0
           dPi(J)=abs(dPdZ)/AveVis*dez*2.0
           Pi(J)=dPi(J)+Pi(J)
           AvePi = AvePi + Pi(J)
           If(J.EQ.1.OR.J.EQ.H) AvePi = AvePi - 0.5*Pi(J)
           Pres(J,2)=Pres(J,1)
           Pres(J,1)=Pres(J,0)
68    CONTINUE
!
        If(Wryte.EQ.Wrytedat) THEN
            AvePi = AvePi/(Real(H)-1.0)
            WRITE(13,'(3X,E15.5,4E12.5,2F9.6)')AvePres,dPdZ,AvePi,&
                &viscosity(50),AveVis,B(100,1,1),B(100,50,1)
            EndIf
            AvePres = 0.0
            AvePi = 0.0
            AveVis = 0.0
!
            DO 85 I = 1,W
                DO 80 J = 1,H
                    T(I,J,1) = T(I,J,3)
80            CONTINUE
85            CONTINUE
!
            DO 87 I = 1,W
                DO 86 J = 1,H
                    B(I,J,0) = B(I,J,2)
86            CONTINUE
87            CONTINUE

```

```

      IF (Wryte.EQ.Wrytedat) THEN
      WRITE(9,'(3X,F8.6,F12.6)') z,T(100,50,1) !Centered Tracer200,100
      Wryte = 0
      ENDIF
!
      If (COUNT.EQ.PRINTNUM.AND.COUNT.LE.Lastprintnum) THEN
      DO 88 I=0,W+1,2
! The 2 means that only every other line of data in the x direction will be printed.
      WRITE(14,'(23X,26F11.6)')&
&T(I,0,2),T(I,2,2),T(I,4,2),T(I,6,2),T(I,8,2),T(I,10,2),T(I,12,2),&
&T(I,14,2),T(I,16,2),T(I,18,2),T(I,20,2),T(I,22,2),T(I,24,2),T(I,26,2),&
&T(I,28,2),T(I,30,2),T(I,32,2),T(I,34,2),T(I,36,2),T(I,38,2),T(I,40,2),&
&T(I,42,2),T(I,44,2),T(I,46,2),T(I,48,2),T(I,51,2)

      88    CONTINUE
!
      WRITE(14,'(X)')      !Should provide a space between each T block
      PRINTNUM = PRINTNUM + Printstep
      Endif
!
      90 CONTINUE
!
      DO 97 I=0,W+1
      WRITE(14,'(23X,52F11.6,6X,24E11.4)')&
&    T(I,0,3),T(I,1,3),T(I,2,3),T(I,3,3),T(I,4,3),T(I,5,3),T(I,6,3),&
&    T(I,7,3),T(I,8,3),T(I,9,3),T(I,10,3),T(I,11,3),T(I,12,3),T(I,13,3),&
&    T(I,14,3),T(I,15,3),T(I,16,3),T(I,17,3),T(I,18,3),T(I,19,3),T(I,20,3),&
&    T(I,21,3),T(I,22,3),T(I,23,3),T(I,24,3),T(I,25,3),T(I,26,3),T(I,27,3),&
&    T(I,28,3),T(I,29,3),T(I,30,3),T(I,31,3),T(I,32,3),T(I,33,3),T(I,34,3),&
&    T(I,35,3),T(I,36,3),T(I,37,3),T(I,38,3),T(I,39,3),T(I,40,3),T(I,41,3),&
&    T(I,42,3),T(I,43,3),T(I,44,3),T(I,45,3),T(I,46,3),T(I,47,3),T(I,48,3),&
&    T(I,49,3),T(I,50,3),T(I,51,3),B(I,1,2),B(I,2,2),B(I,3,2),B(I,4,2),B(I,6,2),&
&    B(I,10,2),B(I,14,2),B(I,15,2),B(I,19,2),B(I,21,2),B(I,22,2),B(I,23,2),B(I,24,2)
      97 CONTINUE
!
      END
!-----
      SUBROUTINE ITdC(TT,BB,det,A1,E1,A2,E2)
!
!   The following set of equations are used to approxiamate
!   the isothermal degree of cure for the vinylester used in this
!   experiment.  T is in Celsius, z is in meters.
!
!   It is known that B(IsoThermal degree of Cure) is zero at the entrance
!   of the die, since Fortran sets all uninitialized variables at zero there is no work to be done.
!
!   The unknown B level is one level behind that of the unknown T level.
!   That is why B goes from 0:2 and T goes from 1:3

```

```

!
DOUBLE PRECISION G, det, k1, k2, k3, BB, TT, BB1, BB2
DOUBLE PRECISION A1, E1, A2, E2
!
k1 = det*G(TT, BB,A1,E1,A2,E2)
!
BB1 = BB + 0.5*k1
k2 = det*G(TT, BB1,A1,E1,A2,E2)
!
BB2 = BB - k1 + 2.0*k2
k3 = det*G(TT, BB2,A1,E1,A2,E2)
!
BB = BB + k1/6.0 + 2.0*k2/3.0 + k3/6.0
!
RETURN
END
!-----
DOUBLE PRECISION FUNCTION G(TT, BB,A1,E1,A2,E2)
!
! The following function evaluates the isothermal rate of cure.
! This is Equation 4 in the paper by Kim, Han and Lee (1997).
!
DOUBLE PRECISION TT, BB, A1, E1, A2, E2
!
G=(A1*DEXP(E1/(TT+273.15))+A2*DEXP(E2/(TT+273.15))*BB**.75)*(1.0-BB)**1.5
!
RETURN
END
!-----
SUBROUTINE TRIDAGY (W, Ay, By, Dy, T, J)
!
! Subroutine for solving a system of linear simultaneous
! The equations are numbered from 1 to H, and their
! sub-diagonal, diagonal, and super-diagonal coefficients
! are stored in the arrays A, B, and C. The computed
! solution vector T(1)...T(H) is stored in the array T.
!
DOUBLE PRECISION Dy(1:200), T(0:201,0:101,3),Ay,By
DOUBLE PRECISION GAMMA(1:200), BETA(1:200)
INTEGER II, JJ, LAST, W
!
! Compute intermediate arrays BETA and GAMMA.
BETA(1) = By
GAMMA(1) = Dy(1)/BETA(1)
!
DO 5 II = 2,W
BETA(II) = By - Ay*Ay/BETA(II-1)
GAMMA(II) = (Dy(II) - Ay*GAMMA(II-1))/BETA(II)

```

```

5 CONTINUE
!
  T(W,J,2) = GAMMA(W)-273.15-Ay*(T(W+1,J,2)+273.15)/BETA(W)
    LAST = W - 1
  DO 10 JJ = 1, LAST
    II = W - JJ
    T(II,J,2)=GAMMA(II)&
    &      -Ay*(T(II+1,J,2)+273.15)/BETA(II)-273.15
10 CONTINUE
  RETURN
  END
!
!-----
!
  SUBROUTINE TRIDAGX (H, Ax, Bx, Dx, T, I)
!
  DOUBLE PRECISION Dx(1:100), T(0:201,0:101,3),Ax,Bx
  DOUBLE PRECISION GAMMA(1:100), BETA(1:100)
  INTEGER II, JJ, LAST, H
!
  BETA(1) = Bx
  GAMMA(1) = Dx(1)/BETA(1)
!
  DO 5 JJ = 2,H
    BETA(JJ) = Bx - Ax*Ax/BETA(JJ-1)
    GAMMA(JJ) = (Dx(JJ) - Ax*GAMMA(JJ-1))/BETA(JJ)
5 CONTINUE
!
  T(I,H,3)=GAMMA(H)-273.15-Ax*(T(I,H+1,3)+273.15)/BETA(H)
  LAST = H - 1
  DO 15 II = 1, LAST
    JJ = H - II
    T(I,JJ,3) = GAMMA(JJ)-Ax*(T(I,JJ+1,3)+273.15)/BETA(JJ)-273.15
15 CONTINUE
!
  RETURN
  END

```

Appendix C

EXAMPLE SCION ANALYSIS

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EXAMPLE SCION ANALYSIS

Using the program Scion Image for Windows, magnified pictures of cross-sections of fiberglass samples were analyzed to determine the void content. The pictures were magnified by two methods: optical microscope and scanning electron microscope (SEM). This appendix shows some of the steps involved in using digital analysis software to measure a property that can be seen. Figure C.2-a shows a picture that was taken with the optical microscope while Figures C.3-a and C.4-a were taken with the SEM. These three examples are of regions of high void fraction. In most of the pictures, the calculated void fraction was nearly zero. However, before showing what voids appear like, Figure C.1 is presented to represent what the approximate void fraction is like. In Figure C.1 the calculated void fraction matched the average void fraction for all the analyzed samples that were pulled at 4 inches per minute.

Figure C.1: Example micrograph of composite material with 0.8% voidage.

Figure C.2-a shows an interface between roving and TH4000 glass mat in a sample that was pulled at 8"/min. The picture was taken at 100X, the lowest magnification of the microscope. The lower magnification improved clarity and increased the field of view. The roving is in the top half of the figure and is parallel to the surface of the picture. The dark circles in the matrix around the roving are glass microspheres, not voids. The dark regions in the mat are considered to be voids. An intermediate step while using Scion Image involves increasing the contrast between the voids and the rest of the picture. Figure C.2-b shows which regions were considered to be voids. After distinguishing which areas are voids, the rest of the picture is deleted so that only the black areas remain. For this particular picture, the next step was to set the scale of 109 pixels equals 210- μ m. The void and photo areas were then measured to determine the void fraction. The void fraction in this picture is higher than average at 2.1%.

Figure C.2-a: Optical Microscope picture of a sample with fibers both parallel and perpendicular to the surface.

Figure C.2-b: Optical Microscope picture of a sample with fibers both parallel and perpendicular to the surface. The voids are identified in black.

While the optical microscope allowed for a large field of view and relatively little time to analyze a sample, the SEM was used to verify that what was being counted as voids with the optical microscope, actually was voids. The pictures in Figures C.3 and C.4 are of regions of relatively high void fraction. Both pictures are at 500X with a current potential of 15,000 volts.

Figure C.3-a shows fibers from the TH4000 mat. In this picture, the fibers, matrix and voids are easily distinguished. Figure C.3-b has the voids contrasted in black. Following similar steps as with the optical sample above, the void fraction for this particular figure is 6.0%. This picture does have the highest void fraction of all the pictures examined, which have the fibers perpendicular to the surface. It was specifically chosen to show examples of voids in this plane.

Figure C.3-a: SEM picture of a sample with fibers perpendicular to the surface

Figure C.4-a also shows a picture of a region of high voidage. This picture is shown as an example of voids in the composite when the fibers are parallel with the surface. Of interest in this figure is a region which could easily be confused as a void, but after careful analysis was considered to be a artifact from sample preparation. The main void in this figure is the dark region that stretches across the entire picture. In the upper left hand region of the figure is a bright region that looks like an indentation in the matrix. The brightness of the region is what indicates this was probably caused by grinding the sample with too much pressure.

Figure C.3-b: SEM picture of a sample with fibers perpendicular to the surface. The voids are identified in black.

Bright regions in a SEM photo are caused by surface charging, which happens when the surface is rough. These rough edges were probably caused when a chunk of matrix was pulled from the composite surface. Figure C.4-b shows the areas that were measured as voids. Using Scion Image, the void fraction of the figure was measured as 6.8%.

Figure C.4-a: SEM picture of a sample with fibers parallel to the surface.

Figure C.4-b: SEM picture of a sample with fibers parallel to the surface. The voids are identified in black.

Appendix D

Pressure Inducing Taper Section

Appendix D

Pressure Inducing Taper Section

A tapered region is generally used at the entrance of the die to facilitate the correct alignment of the reinforcing fibers. Under particular conditions the tapered region will also serve to pressurize the resin before it enters the main part of the die (assuming a geometry similar Figure D1). This section outlines the calculations that are used to determine the pressure generated by a particular shape of taper and then covers how the additional pressure affects the pressure function.

Fluid Mechanics

Figure D1 represents a cross section of the Even-Leg Angle die. As shown in the figure, the tapered region on this die is a separate manifold that attached to the front faces of the top and bottom sections of the die. Unseen in the figure is the fact that the manifold (tapered region) does not wrap around to include the sides. Therefore, the following discussion does not apply to the experimental setup for this research, but could be used to further improve the design.

In a die where the tapered region completely surrounds the circumference of the die, two phenomena can occur in the tapered region. Excess resin is forced to flow backward, out of the die, because of the change in cross sectional area. At the same time, the forced flow of resin causes pressure to develop within the resin. These phenomena are directly related and can both be used to benefit the final product. First, consider the mechanically induced flow of excess resin countercurrent to the direction that the fibers are being pulled. This flow can work to fill some of the voids that still remain in the fibers. If a region of fibers passes through the resin bath without being contacted with resin, it will enter the taper and confront a flow of resin that may push the

Figure D1: Pultrusion Die with a tapered zone

void out of the fiber bundle. However, by experience it is known that the even with the tapered section in the die, the product still ends up with voids. The second phenomena, mentioned above, can be used to further decrease the void fraction.

The pressure that is created near the die entrance will be used to fill the voids that normally do not get filled. This will be accomplished by optimizing the pressure function of the product. The following part of this section is designated to show how the flow of resin can be modeled.

Model Formulation

Tapered regions are normally short (about five centimeters for a one-meter long die) and very little heat transfer takes place between the die and the composite; therefore the temperature of the resin is effectively constant during this region. So, for the tapered section, it is assumed that pressure is only developed from the flow of resin relative to the fibers. After the tapered section, the die maintains a constant cross-sectional area so there are no mechanical forces that tend to

cause the resin to flow. Throughout the rest of the die, the resin quickly heats, cures, releases energy, and cools. Earlier chapters were dedicated to this analysis.

Increasing the resin pressure through the tapered zone is described in part by the fluid pressure drop equation represented by Darcy's law for fluid flow in a porous medium.

$$Q_f = - \frac{k_z A_{xs} \Delta P}{\eta z_{taper}} \quad (D.1)$$

Where volumetric flow rate Q_f is a function of the permeability k_z , viscosity η and the pressure drop, ΔP . A_{xs} and z_{taper} are the cross sectional area for flow and the length of the flow region respectively. The viscosity of the resin is assumed to be Newtonian. Therefore, while in the tapered section the viscosity is constant since the temperature does not change. Gupta³ derived Darcy's Law for use in describing polymers. In order to apply Eq. D.1 to a moving bed, the equation must be modified to maintain an Eulerian frame of reference. The flowrate is defined as the net superficial flow minus the flow carried with the fibers. The equation is also written in differential form for integration purposes. With the previous modifications, Eq. D.1 becomes

$$q - (1 - V_f)v_z = - \frac{k_z}{\eta} \frac{dP}{dz} \quad (D.2)$$

where q is the velocity of flow and V_f is the volume fraction of fibers in the finished product. The Kozeny-Carman relation⁴, which is described in terms of the fiber volume fraction and the fiber diameter, is useful to determine the bed permeability (for flow in the direction of fiber orientation)

$$k_z = \frac{D_f^2}{16K} \frac{(1 - V_f)^3}{V_f^2} \quad (D.3)$$

³ R. Gupta, "Flow Through Porous Media," Polymer and Composite Rheology, 2nd Ed., Marcel Dekker, NY, (2000) Chapter 16.

⁴ G. Batch, "Crosslinking Free Radical Kinetics and the Pultrusion Processing of Composites," PhD Thesis, University of Minnesota, Minneapolis, Minnesota (1989).

K_z is the Kozeny constant and is set as 1.4 for this work. In general it is larger than 0.5, increasing with more closely packed fibers. By applying Eq. D.2 to the tapered zone geometry and including Eq. D.3 the pressure gradient is

$$\frac{dP}{dz} = \frac{16K_z \mu}{D_f^2} \frac{V_f^2(\mathbf{z})}{[1 - V_f(\mathbf{z})]^3} [1 - 2V_f(\mathbf{z})] \quad (\text{D.4})$$

where $\frac{V_f(\mathbf{z})}{V_f(1)} = \left\{ 1 + \left(\frac{h(0)}{h(1)} - 1 \right) (1 - \mathbf{z}) \right\}^{-1}$

for a taper of linear shape. The separation between the two die plates is $h(0)$ at the beginning of the taper and $h(1)$ at the end of the taper zone. The value of $h(1)$ also corresponds to the height of the die after the tapered region. The dimensionless distance into the taper zone is ζ .

A sample pressure profile for resin in a tapered region is presented in Figure D.1. The parameters used for this profile are shown in Table D.1. From Figure D.1, notice that the pressure builds nearly linearly with distance into the die. For this case, a total of about 275-psi is created. Under more extreme conditions, such as high glass content, high resin viscosity, or small fiber diameter, the profile can become nonlinear. Under these conditions it could be of value to explore different taper shapes. It was not determined whether the shape of the pressure profile has an influence on the final properties of the composite. It is good to point out that the final pressure is a function of many things: taper shape, pull speed, resin viscosity, fiber diameter, fiber volume fraction, and bed permeability.

If the tapered region of the Equal Leg Angle die had sides added to it, then it could also be used to increase the pressure in the die. Figure D.1 shows a very optimistic taper pressure profile. These calculations were based on an even distribution of fibers; all being evenly compressed to cause the resin backflow. The fiberglass in the Equal Leg Angle part (and most

Figure D.1: Tapered Region Pressure Profile

Table D.1: Parameters for pressure profile in Figure D.1

Kozeny constant	K	1.4
Viscosity	η	0.88 Pa-s
Pull speed	v_z	30.5 cm/min
Average fiber diameter	D_f	0.00141 cm
Final glass volume fraction	$V_f(1)$	0.4653
Initial taper gap	$h(0)$	1.029 cm
Final taper gap	$h(1)$	0.953 cm
Taper length	z_{taper}	7.62 cm

other parts used for structural applications) is significantly comprised of mats. These mats are either stitched or woven together. In either case, the fibers are more tightly packed than normal roving. If the taper pressure is recalculated assuming that the mats are already compressed before entering the tapered region, then the final taper pressure is about 50 psi. About half of the decrease is accounted for by the change in average fiber diameter. The average diameter of all the fibers is $14.1\mu\text{m}$, while roving diameter is $20\mu\text{m}$.

By including an estimated 50 psi from the tapered region, the Pressure Function increases from the 5.0×10^7 for the case at $8''/\text{min}$ in Figure 7.9 to 6.5×10^7 .

Conclusions

It was shown that the Pressure Function can be increased without changing the current operating conditions. This is good for improving the product if all other conditions are already optimized. The method involves adding a tapered region at the entrance of the die. The tapered region can be $0 - 20^\circ\text{C}$ above ambient temperature, but more importantly is geometrically designed to pressurize the resin as it enters the die. The total pressure developed by the taper, influences the nature of the composite until it shrinks (due to the resin curing) completely away from the die. Depending on the processing conditions, the composite normally shrinks away from the die in the second half of the die.

The entrance of the die should be fitted with a tapered region. The current Equal Leg Angle die already uses a partial tapered region. It merely need to have sides attached to the top and bottom plates so that pressure will develop.