DEVELOPMENT AND VERIFICATION OF A THERMAL MODEL FOR CURVED-LAYER LAMINATED OBJECT MANUFACTURING OF POLYMER MATRIX COMPOSITES

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DEVELOPMENT AND VERIFICATION OF A THERMAL MODEL FOR CURVED-LAYER LAMINATED OBJECT MANUFACTURING OF POLYMER MATRIX COMPOSITES

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A thermal model of the Curved-layer Laminated Object Manufacturing (Curved LOM) process was developed. This process consists of layer-by-layer heated lamination and laser cutting of sheet material to build curved or flat prototype components. The model was based on one-dimensional transient heat conduction with heat production due to chemical reaction within the part. To simplify the model development, rectangular geometry and building of flat layer parts were assumed. These assumptions are considered reasonable for heat transfer in curved parts with shallow curvature. Heat produced from the processing of advanced composite materials was also included in the model formulation. Estimation of the heat production occurring within the part requires the kinetic modeling of the exothermic cure reaction. The cure reaction was modeled with autocatalytic reaction kinetics typical of epoxy resins. A kinetic analysis of a glass/epoxy prepreg was performed as a part of the study. With the kinetic model included, the overall Curved LOM model was able to predict temperature and cure distributions throughout the material during the process simulation.
To verify the model, a series of 20-layer parts was built in a layer-by-layer cycle that simulated the actual Curved LOM machine. Thermocouples were embedded in the part every fourth layer to record temperature during the process. Two material systems were selected to isolate and verify the key aspects of the Curved LOM model. The first material, a monolithic SiC ceramic tape material, was used to verify the internal heat conduction portion of the model. The overall Curved LOM model that included heat production was verified by a prepreg system comprised of a glass fiber cloth impregnated with an epoxy resin. In both cases, the model predictions of the experimental data were accurate for a majority of the observed response.
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NOMENCLATURE

a \hspace{1cm} \text{thermal diffusivity (cm}^2 \text{sec}^{-1})

A_1 \hspace{1cm} \text{frequency factor for rate constant 1 (sec}^{-1})

A_2 \hspace{1cm} \text{frequency factor for rate constant 2 (sec}^{-1})

C_p \hspace{1cm} \text{heat capacity of build material (Jg}^{-1} \text{K}^{-1})

E_1 \hspace{1cm} \text{activation energy for rate constant 1 (J mol}^{-1})

E_2 \hspace{1cm} \text{activation energy for rate constant 2 (J mol}^{-1})

h_{\text{air}} \hspace{1cm} \text{heat transfer coefficient, part to air (Wm}^{-2} \text{K}^{-1})

h_{\text{lam}} \hspace{1cm} \text{heat transfer coefficient, part to laminator (Wm}^{-2} \text{K}^{-1})

h_{\text{base}} \hspace{1cm} \text{heat transfer coefficient, part to base plate (Wm}^{-2} \text{K}^{-1})

\Delta H_p \hspace{1cm} \text{total material heat of reaction (Jg}^{-1})

k \hspace{1cm} \text{thermal conductivity of build material (Wm}^{-1} \text{K}^{-1})

k_z \hspace{1cm} \text{thermal conductivity of build material in z-direction (Wm}^{-1} \text{K}^{-1})

k_1 \hspace{1cm} \text{rate constant 1 (sec}^{-1})

k_2 \hspace{1cm} \text{rate constant 2 (sec}^{-1})

R_p \hspace{1cm} \text{polymerization reaction rate (= d}\alpha/dt \text{) (sec}^{-1})

\text{t} \hspace{1cm} \text{time (sec)}

T \hspace{1cm} \text{temperature (°C)}

T_{\text{air}} \hspace{1cm} \text{temperature of air surrounding part (°C)}

T_{\text{bottom}} \hspace{1cm} \text{temperature of part bottom surface (°C) (note } T_{\text{bottom}} = T_0 \text{ in Figure 4)}

T_{\text{base}} \hspace{1cm} \text{temperature below LOM-paper base (°C)}
\( T_{\text{lam}} \)  temperature of laminator (°C)

\( T_{\text{surface}} \)  temperature of part top surface (°C) (note, top surface location changes as layers are added)

\( V_f \)  volume fraction (dimensionless)

\( z \)  spatial coordinate, through the thickness of the part (cm)

\( \alpha \)  degree of cure (dimensionless)

\( \rho \)  density of build material (g/cm^3)
CHAPTER I
INTRODUCTION

In this opening chapter, the evolution of Laminated Object Manufacturing (LOM) as well as the Curved Layer Laminated Object Manufacturing (Curved LOM) process is reviewed. Introductory information on the cure of thermosetting polymers is also presented. Finally, the objectives of this work are defined.

1.1. Curved LOM Background

Laminated Object Manufacturing (LOM) belongs to a family of processes known as Rapid Prototyping (RP) or Solid Freeform Fabrication (SFF). These processes share several distinguishing features. The primary similarity is the fabrication of three-dimensional physical prototypes from the sequential addition of two-dimensional cross-sections. A three-dimensional Computer Aided Design (CAD) file of the object to be manufactured is converted to a tessellated file format (.STL) that approximates the surface of the solid object with a network of adjacent triangles. Next, RP software algorithms "slice" the .STL file into a series of horizontal layers. "Slicing" is accomplished by intersecting the solid object with horizontal planes. The points on the plane that intersect with the object define the two-dimensional cross-section of the object at a specific height. This information can be used to control machine paths required to physically reconstruct the cross-sections by depositing, solidifying or cutting material.
These planar cross-sections, when stacked upon one another, produce the full-scale three-dimensional prototype of the desired part.

The LOM process was developed by Helisys, Inc. [1]. A schematic of the process is shown in Figure 1. LOM is based on a fully automated, repeating cycle of feeding, bonding, and cutting layers of sheet material. The process builds parts by laminating sheets of adhesive material (i.e., adhesive paper or thin plastic) and cutting out the cross section of the part in the layer. Each layer is adhered to the previous layer using a heated roller in the forward and reverse directions. Then, a CO₂ laser cuts out the cross section of the part and dices the remaining material so that it can be removed when the part is completed. However, during the build, the excess material serves as supporting material for the part throughout the build. Several advantages of the LOM process in comparison to other traditional forms of prototype manufacture include minimal limitations on allowable part geometry, no need for a mold or tool in which to manufacture the part, and the mode of manufacture is relatively inexpensive compared to other methods of prototype manufacture. However, there are also some difficulties to be considered. The part to be produced must be obtained as a three-dimensional CAD file, and for parts with complex curvatures, the surface finish of the final part is not smooth due to the repetitive layering of flat sheets.

Early (c.a. 1990) application of the LOM process was for creating full-scale paper prototypes of parts. These prototypes were suitable for verifying designs and testing form, fit and function. During the middle and late 1990’s, significant advances have produced the capability of fabricating advanced material prototypes and end-use components from ceramics [2, 3] and fiber composites [4, 5, 6]. However, the desire to
use this process to manufacture parts from advanced materials, such as ceramics and composites, has magnified the previous disadvantages and created others. For example, for composite panels with curvature, the optimum strength can be attained when the fiber reinforcement is oriented in the direction of curvature. With LOM, the user is constrained to building with flat layers only, thus destroying the continuity of the reinforcement and significantly reducing the strength below the potential strength of the part. Also, a substantial amount of waste is produced.

Figure 1: Schematic of the Laminated Object Manufacturing process (Helisys, Inc.)

To address these difficulties, several modifications were made to the standard LOM process. The results of these adjustments produced a new novel RP process known as Curved-Layer Laminated Object Manufacturing (Curved LOM). The concept behind Curved LOM is nearly identical to the standard LOM process, but the means by which
the physical reproduction of the part is accomplished is somewhat different. The details behind these changes can be found in the literature [7]. The stages of the Curved LOM process are shown in Figure 2. The process of cyclic lamination and cutting remains the same. The lamination of the parts is accomplished via a conformable rubber bladder that contains a flexible heating pad. A schematic of this laminator is shown in Figure 3. The process of laser-cutting the cross-section of the curved part is accomplished in the same fashion as the standard LOM process except the platform also moves to account for the changes in part height during the manufacture of curved parts [7]. Layer placement is accomplished manually of via a vacuum-assisted pickup mechanism that is connected to the laminator pad (not shown in Figure 3).

Figure 2: Process steps for Curved-Layer Laminated Object Manufacturing.
Through of the development of the Curved LOM process, surface finish and fiber orientation problems that are encountered using the standard LOM have been practically eliminated. Also, the use of this process has also resulted in less material usage for curved parts and shorter manufacturing times than the standard LOM process. However, there is a requirement that the curved part be manufactured upon a curved tool or base. From the results of a previous study (see Appendix A), it was concluded that this base could be manufactured via the standard LOM process using the normal LOM adhesive paper. So, the process of producing full-scale curved panels using the Curved LOM process does not require one to leave the realm of RP (i.e. tool-less processes) to achieve this objective. The Curved LOM process has been demonstrated to build parts from ceramic matrix composites (CMC’s) and polymer matrix composites [8, 9].

**Figure 3**: Cross sectional schematic of Curved LOM laminator and platform (not to scale).
Thermoset polymers fall into a class of polymers known as network polymers. These are polymers in which three-dimensional linkages are formed throughout the bulk of its structure. Thermosets in particular have a high density of these network connections, which are commonly known as crosslinks. The reactions that cause these crosslinks to form are collectively known as thermoset cure. When cure proceeds to the full extent in thermosets, a high degree of crosslinking and entanglements are present in the structure of the substance. Macroscopically, the physical characteristics of thermosets are particularly favorable for load-bearing applications. These physical characteristics include insolubility, dimensional stability, and infusibility. Common thermosets, such as epoxies, phenolics, polyesters, polyimides, and bismaleimides, are most often found in coatings and adhesives for various applications. However, because of the nature of their processing and the physical nature of their initial and final states, thermosets have become and are still popular as matrices for advanced composites.

Curing of thermosetting polymers, as well as other network polymers, is a process of polymerization. During cure, there is an increase in the average molecular weight of the polymer. The cure reaction is usually an exothermic reaction; but like many other reactions, the cure process requires an initial supply of energy. This supply of energy can come in several forms. The two that are used most often are thermal energy and light energy. Thermosets that are cured by energy supplied from a light source are called photopolymers. Generally, the type of light that is used in photopolymerization is ultraviolet light. However, most thermosets are cured through the use of heat energy.
Thermoset polymerization (i.e. cure) does not occur in the same fashion as the polymerization of thermoplastic polymers. Thermoplastics are linear polymers. This means that the polymer chains grow as independent threads. These threads can be physically entangled, but they are not chemically linked. The crosslinked networks formed in a thermosetting polymer grow in three dimensions by chemically linking between linear threads as the reaction proceeds. This is what causes the fundamental property differences between thermosets and thermoplastics. From a chemical standpoint, the monomer functionality defines whether chemical crosslinking can take place in a polymerization reaction. Monomer functionality refers to number of molecular linkages that a monomer can make with other molecules. The monomers of linear polymers (thermoplastics) have a monomer functionality of two, meaning that monomer can only link to two other reactive sites. The reactions can be with a polymer chain, another monomer or to a terminating reactant. Monomers with functionality higher than two have additional reactive sites to continue further polymerization after linear polymerization takes place. When these sites line up, they can form crosslinks between the polymer chains and thus form the three-dimensional networks characteristic of thermosets [10].

The physical nature of chemical crosslinking is quantified and represented by two fundamentally different, but conceptually equivalent measurements. The most definitive value to represent cure is the crosslink density. The crosslink density is a quantitative measure of the number of crosslinks that exist in a given volume in the thermosetting polymer. This value is related in some fashion to the degree of cure. The degree of cure does represent a certain level of chemical crosslinking in the thermoset, but the value
obtained for the degree of cure is relative. This means that the uncured and fully cured states on the material must be defined to determine the degree of cure. Because the chemical reaction that occurs during thermoset is often exothermic, the initial and final cure states are determined by measurements of the heat released during the cure process. Once these limits have been characterized, the degree of cure and the crosslink density become directly related. Thus the chemical crosslinking in a thermoset polymer corresponds to the physical nature of the polymer’s cure.

Since the crosslink density of a polymer network is an absolute quantity, the only means by which the relationship between crosslink density and the degree of cure can be defined is from direct measurement of the crosslink density of the polymer network. There are a number of ways that the crosslink density can be directly determined in a polymer network. One method involves the use of Pulsed Nuclear Magnetic Resonance (NMR) spectroscopy. In most cases, NMR is used to measure the short-range or long-range cooperative motions of polymer chains in the crosslinked network and relate the measured relaxations to crosslink density. However, some cases do exist where NMR is used to directly detect the polymer crosslinks. The other method used to directly determine crosslink density is through the use of solvent swelling. It has been determined that the extent of swelling is inversely proportional to the crosslink density of a network polymer. This fact has made this technique one the most widely used techniques in studying crosslinked polymer networks. Several relationships between the degree of swelling, rate of swelling, and the crosslink density. The two techniques described here are further explained in the literature [11].
Optimizing the curing of thermosets requires an intimate knowledge of the chemical kinetics of the polymerization and crosslinking reactions. This information is necessary to tune the parameters of the technique that will be used to cure the polymer. The parameters that define the cure technique (e.g., time, temperature, light intensity, etc.) ultimately determine the final physical properties of the polymer. Once the kinetics are understood and the actual chemistry behind cure is established, these cure parameters can be chosen based on the desired polymer properties. Usually, the goal of the process seeks to achieve a certain degree of cure, which is also quantified by means of the extent of reaction. For thermal curing polymers, these quantities can be calculated based on data from thermal analysis and the stoichiometry of the polymerization reaction. Articles by Levy and Gill [12], Manley and Scurr [13] as well as from Stark and Seferis [14] describe these thermal analysis techniques in detail and discuss their relevance to the characterization of thermosets. An overview and description of the relevant analytical techniques and their importance in the characterization of thermosetting polymers is discussed in a later section of the thesis. These techniques will be used to characterize some of the properties of materials used in this research.

1.3 Problem Statement

The objective of this study is to develop a mathematical model of the thermal aspects of Curved LOM that will predict the temperature and cure distribution of the manufactured part throughout the building process. In so doing, the key aspect of the objective is to be able to simulate the manufacture of polymer composite materials. In previous research, the feasibility of producing functional composite parts via the standard
LOM process and the Curved LOM process was established [8, 9]. Also, modeling of the standard LOM process has been completed and analyzed [15, 16]. Building on these previous efforts, two major activities are required to achieve the objectives of the current work. First, the model of the standard LOM process, which is discussed in section 2.2 of this thesis, must be modified to accommodate the differences attributed to the Curved LOM process. Secondly, the thermal aspects of polymer cure must be examined and integrated into the model so that the model can account for the curing of the composite materials during manufacture. Included in this research are the model development, material selection and assessment, as well as model verification procedures.
CHAPTER II

REVIEW OF LITERATURE

In this chapter, a review of the relevant literature is provided. Subjects include solid freeform fabrication of advanced materials, modeling of the LOM process, kinetic modeling of epoxy resins, and the thermal modeling of autoclave/vacuum-bag consolidation of composite materials.

2.1. Solid Freeform Fabrication of Advanced Materials

Solid Freeform Fabrication techniques have been considered practical processes for rapidly producing full-scale prototypes of parts. Additional efforts have been made over the past decade to apply these techniques to the manufacture of functional parts made from advanced materials such as ceramics, metals, and fiber composites. Some of these efforts have been fueled by the lack of a fully automated process for producing complex-shaped parts from these materials. Also, many people have sought to obtain parts from these processes that can be tested as if they were full production-grade parts while still maintaining the advantage of rapid manufacture. The use of these RP techniques to produce functional ceramic and composite parts has become an interesting area of research.

The first commercially available RP technique to demonstrate the ability to produce functional ceramic parts was the Selective Laser Sintering (SLS) process. In the SLS process, a thin layer of heat-fusible powder is spread across the machine platform
using a roller. A solid area of required shape is created in this layer of powder by rastering a laser beam on the surface. This action fuses the loose powder to the surrounding particles in the surface layer as well as the layer below. A new layer of the powder is then spread and the process repeats itself until all layers have been created. Similar to the LOM process, the excess material remains in place during the process to support the part, and it is removed after completion of the cycle. Originally, the process was intended to make prototypes from waxes and thermoplastic polymers. Lakshminarayan, Ogrydziak, and Marcus [17] first demonstrated the production of ceramic prototypes from the SLS process. In this research, a two-phase system consisting of alumina and aluminum phosphate was used to manufacture parts. Since that time, subsequent attempts to produce metal [18] and particulate-reinforced metal matrix composite [19] prototypes using the SLS process have been made. In these cases, the grains of build material were encapsulated in a polymeric binder that melted during laser irradiation. Subsequently, binder burnout and densification stages were needed to produce fully useable components.

Stereolithography (SLA) is the most commonly recognized SFF technique. The prototypes are made from a photo-curable thermosetting resin. The liquid resin resides in a vat. A platform is lowered into the resin vat until a thin layer of the liquid monomer covers it. An ultraviolet laser beam is then rastered on the surface of the resin layer to cure a cross-section of the prototype and bond it to the platform. The platform is then lowered by one layer to allow the resin to cover the previous layer. The next layer of the prototype is then cured and the cycle repeats itself until the final prototype is completed. Griffith and Halloran [20] were able to demonstrate that SLA could produce ceramic
prototypes. The process made prototypes from what was termed a “ceramic resin,” which consisted of a ceramic powder suspended in a UV-curable resin. The composition of the suspension was generally between 40 and 60 weight percent ceramic. Suspension of the ceramic powder in the resin was found not to be problematic. However, because of the opacity of the ceramic suspension, it was found that viscosity and cure depth were critical in determining whether certain ceramics could be used. Also, light scattering has been determined as an issue in relation to part accuracy. These concerns have been characterized and reported [21, 22]. When the cure depth is acceptable, the production of green ceramic parts via this process is feasible. The results of the densification have been reported as favorable.

Fused Deposition Modeling (FDM) was the next commercial RP technique used to produce functional prototypes from advanced materials. Production of prototypes using the FDM process is somewhat different that the previously discussed SFF techniques in that the prototypes do not require waste material removal. Filaments of a low temperature melting material, such as a wax or thermoplastic polymer, are metered into the FDM machine and extruded through a small heated nozzle onto a platform. The nozzle delivers the extruded material to the required areas by rastering in the x-y plane as determined by the computer calculated geometry derived from the .STL file. The platform upon which the material is deposited translates in the z-direction by one layer thickness with each new layer until the build is complete. Agarwala et al. [23] were able to produce ceramic components using Fused Deposition of Ceramics (FDC). In the FDC program, the feedstock was modified such that silicon nitride powder was mixed into the low temperature melting polymers used for FDM. The polymer acted as the carrier for
the ceramic powder during the prototype build stage. Following the build, standard ceramic techniques for densification were applied to obtain the fully dense ceramic part. Further developments were made to produce metallic prototypes as well [24]. Improvements in feedstock quality and machine adjustments made to aid extrusion of the material have led to the production of parts that have a significantly high quality [25].

There have been efforts to use the LOM process to fabricate prototypes with ceramic and composite materials. Griffin, Mumm, and Marshall [26] demonstrated the use of the standard LOM process in the fabrication of monolithic ceramic prototypes. They used formulations of monolithic zirconium oxide and composite ZrO2/Al2O3 in tape-cast sheets as the laminating material. The results showed that green ceramic parts could be easily manufactured via the standard LOM process. Priore [4] showed the feasibility of producing polymer composite parts using the LOM process. This was accomplished by laminating and cutting prepregs consisting of fiber reinforcement and a polymer matrix. Klosterman et al. [2, 27] continued to develop the LOM process to produce monolithic silicon carbide ceramic and ceramic matrix composite (CMC) parts. In their work, they noted that the fiber orientation in complex-shaped CMC’s needed to follow the direction of curvature. This led to the direct development of the Curved LOM process [8]. Thus, net shape freeform CMC’s could be produced using this process along with a post-densification stage.

While these commercial SFF techniques have demonstrated the capability of producing functional prototypes from advanced materials, other processes have been specifically developed to produce similar components from advanced materials. Yoo et al. [28] demonstrated the production of advanced ceramic components using the Three
Dimensional Printing process. Greulich, Greul, and Pintat [29] created green ceramic parts using the Multiphase Jet Solidification process. Hilmas [30] developed Extrusion Freeform Fabrication, a modification of FDM. The process was then used to produce ceramic and thermoplastic polymer components [31]. A gas-based RP process known as Selected Area Laser Deposition was shown to be able to produce titanium oxide parts by Jakubenas et al. [32]. Finally, Cawley et al. [33] demonstrated that the CAM-LEM (Computer Aided Manufacturing of Laminated Engineering Materials) process is able to produce layered ceramic and composite parts. Other than the LOM process, this is the only process that has the potential to process fiber reinforced composite laminates.

The high level of interest in commercial and developmental SFF techniques that are able to produce prototypes from advanced materials shows the importance of this research. In many cases, it is difficult to rapidly produce complex, functional parts from advanced materials such as ceramics, ceramic matrix composites, metal matrix composites, and polymer matrix composites. Methods for producing these parts quickly are at a premium. Curved LOM is one of the developmental processes that can produce functional components from advanced materials. An analysis of this process in a rigorous and theoretical manner will help guide process improvements that can potentially lead to a high quality process for rapidly producing functional components from these types of materials.
2.2. LOM Process Modeling

Several models to date [15, 16, 34, 35] have been developed for the standard LOM process (see Figure 1). The original impetus for modeling the LOM process was for optimization of the manufacture of paper prototypes. With the establishment of research on the use of LOM for advanced materials, the modeling of the general characteristics of the lamination and laser cutting processes has taken on an increased level of importance. In general, models of the LOM process are primarily used to optimize lamination and to introduce intelligent control to the process. The lamination of the material is critical in achieving the necessary part integrity.

The thermal and mechanical aspects of the lamination stage play the most important role and are generally the aspects that are considered by most LOM models. The importance of these aspects is fairly intuitive. From a mechanical point of view, without the appropriate level of contact and mechanical adhesion in the construction material, lamination cannot occur. The laminator must apply the appropriate amount of heat and pressure to obtain the optimum level of adhesion. Since heat addition plays a role, the temperature of the laminated part also has an effect on lamination. Too low a part body temperature can lead to poor adhesion of the individual layers, which may result in delamination in the final prototype. If the part body temperature is too high, the part can yield excessively in compression or shear. This can lead to a lack of both structural rigidity and dimensional accuracy in the final part.

Pak and Nisnevich [34] developed an empirical mathematical model to improve the lamination efficiency of the LOM process. The model uses a pseudo-steady state approach to estimate a minimum heater temperature for adequate lamination based on the
roller speed, material deformation, and material physical properties. The model inadequately accounts for material thermal properties; nonetheless, the results do provide a basis for using the model as a means for improving lamination efficiency.

The thermal phenomena occurring in the part is determined with a model developed by Flach, Klosterman, and Chartoff [15]. The model predicts the temperature distribution within the part body during the part building process. Primarily, the goal of these predictions is to relate material behavior and lamination during the build cycle to system inputs that can be manipulated via process control algorithms. The model determines the transient thermal behavior of the part due to the heat added by the roller and heat loss to surrounding air and base plate, which can all be controlled. The governing equation for three-dimensional heat conduction was solved using a finite difference approximation method. Verification of the model was then accomplished experimentally in the LOM process by placing thermocouples on every fourth layer of the lamination process. The results show strong qualitative and quantitative agreement between the results of the model and the experiment. In subsequent research, Flach et al. [16] used model simulations to gain insight into the effect of the parameters on the ultimate part temperature through the part building cycle.

Sonmez and Hahn [35] take both the thermal and mechanical features of the LOM process into account in their mathematical model. A fully coupled finite element modeling (FEM) approach was used to estimate the temperatures and the stress distribution within the part. The thermal model was coupled with the stress analysis to examine the thermomechanical effects on lamination during the build process. Model results were then used to analyze lamination from the point of view of material transitions
(e.g. melting) and deformation at the top of the part block. The results showed the effects of process parameters that cannot be varied readily in the commercial LOM systems such as roller size and the use of compaction shoes. The parameters that were examined in this study may certainly help one to design a new machine to perform the lamination process. However, the results do not emphasize or relate to the effect of parameter changes that can readily be made in a standard LOM machine such as platform retract, which defines the amount of force that the part sees from the roller, and roller speed.

2.3. Kinetic Modeling of Epoxy Resins

An extensive and detailed review of the literature on modeling of cure kinetics for thermosetting polymers was presented by Prime [36]. While this reference gives a broad review of the modeling of all thermosetting polymers, this thesis will specifically address the modeling of epoxy resins. The kinetic modeling of these polymers is needed in order to account for the heat produced by an epoxy composite prepreg in an overall model for the Curved LOM process.

Kinetic analyses seek to determine the relationship between the rate of reaction and other parameters that have a significant effect on the reaction rate. In most cases, these parameters are the temperature and the reactant concentration. Since it can be physically difficult to measure or determine an accurate value for the concentration of the thermoset reactive groups, the concentration is represented by the degree of cure, which represents the fractional conversion of the monomer to polymer. The temperature of the reaction is factored into the reaction rate equation by a temperature dependent rate constant. Thus, the chemical kinetics of thermosets generally represented by:
\[ \frac{d\alpha}{dt} = k(T)f(\alpha) \]  

(1)

where \( \frac{d\alpha}{dt} \) is the reaction rate, \( \alpha \) represents the degree of cure, and \( f(\alpha) \) is a function that solely depends on the degree of cure [35]. The changes in the kinetic rate constant, \( k \), with temperature is modeled as function by an Arrhenius expression of the form:

\[ k_i(T) = A \exp \left( \frac{-E_i}{RT} \right) \]  

(2)

These relationships are then used to relate the conversion to temperature and time variables. Once these relationships are obtained, the conversion can then be related to other important quantities such as viscosity, glass transition temperature, and cure cycle time.

Models for the chemical kinetics of epoxy resins generally fall into one of two categories based on the mechanism of the cure reaction. Often, when the reaction rate is highest at the start of the reaction (given an isothermal system temperature), the kinetics is modeled by a simple nth-order kinetic expression. Other reactions can accelerate to a certain degree as the reaction proceeds. These reactions are termed as autocatalytic reactions. Typical empirical expressions for the various models of epoxy cure kinetics are listed in Table 1. These kinetic model equations are based upon experimental observation of typical, commercial amine-cured epoxy reactions. It is also possible to develop a kinetic relationship for the cure reaction by examining the mechanism of the reaction. Such mechanistic models for amine-cured epoxy resins have been investigated by Chiao [37] as well as Lai et al. [38].
Table 1: Empirical Kinetic Models for Epoxy Cure

<table>
<thead>
<tr>
<th>nth-order</th>
<th>Autocatalytic</th>
</tr>
</thead>
<tbody>
<tr>
<td>[ \frac{d\alpha}{dt} = k_1 (1 - \alpha)^n ]</td>
<td>[ \frac{d\alpha}{dt} = k_1 \alpha^n (1 - \alpha)^n ]</td>
</tr>
<tr>
<td>[ \frac{d\alpha}{dt} = (k_1 \alpha + k_2)(1 - \alpha)(B - \alpha) ]</td>
<td></td>
</tr>
<tr>
<td>[ \frac{d\alpha}{dt} = (k_1 \alpha^m + k_2)(1 - \alpha)^n ]</td>
<td></td>
</tr>
</tbody>
</table>

Determination of the kinetic parameters requires one to monitor the cure reaction. Specifically, the degree of cure must be monitored as a function of time and temperature as the reaction progresses. Because the degree of cure is not directly measurable, a quantity that is measurable must be related in some form to the degree of cure. One common approach for relating a material characteristic to the degree of cure is by measuring the heat of reaction. This approach is valid if the assumption of no side reactions is true. The primary method for monitoring cure of thermosets (via the heat of reaction) is through the use of a thermal analysis technique known as Differential Scanning Calorimetry (DSC). DSC measures heat flow to and from a specimen as a function of time and temperature. A more complete description of DSC is given in a later section of the thesis. Duswalt [39] describes the various methods for using DSC to obtain kinetic parameters, including isothermal methods and programmed rate methods.

Often, the kinetic modeling of epoxy resins is performed to allow the determination of thermal aspects of the processing of these polymers in composite materials. For example, Shanku et al. [40, 41] used a kinetic model for an epoxy system to evaluate resin flow and composite consolidation in the pultrusion process. The results in their analysis showed they could predict viscosity reasonably well despite inaccuracies that were apparent in the cure model analysis. Numerous examples exist of the use of
kinetic models in autoclave/vacuum-bag cure of laminate composites. An example is the modeling of degree of cure in a standard aerospace epoxy resin by Lee et al. [42].

2.4. Thermal Modeling of Autoclave Consolidated Composite Materials

As mentioned previously, the kinetic modeling of thermoset polymers can be used to estimate certain thermal characteristics during composite processing. Many composite manufacturing processes have been modeled, including resin transfer molding (RTM) and pultrusion. However, the process that most resembles the Curved LOM process is vacuum-bagged, autoclave cure of composite prepreg lay-ups. To gain a greater understanding of material issues that may be encountered in this process, the thermal modeling of vacuum-bagged composite materials and its relationship to Curved LOM processing of composite materials are examined.

Loos and Springer [43] developed a comprehensive model of the cure of autoclave consolidated epoxy matrix composite materials. The model consisted of a one-dimensional heat transfer model, a kinetic cure model, a resin flow model, a void formation model, and a stress distribution model. Model solutions were obtained via unspecified numerical methods. The heat transfer and resin flow models were experimentally verified using a conventional cure cycle on 64-ply composites subjected to various pressure applications. The results obtained from the thermal model agreed with results from experiment. The resin flow model showed good agreement with experimental measurements. The model was then used to prepare a methodology for optimizing autoclave cure cycles.
A model was developed by Saliba et al. [44] to investigate transient heat transfer and crystallization in PEEK thermoplastic polymer composites during the consolidation process. The model uses a body-fitted-coordinate grid generation system in conjunction with the finite difference method to solve the two-dimensional energy equation. The complete model predicts temperature and crystallinity distributions in complex-shaped, autoclave-consolidated thermoplastic composites. The results of the model predictions were verified with published data. This model was extended to apply to thermosetting composites [45, 46]. In the case of the thermoplastic composites, crystallization kinetics determined the amount of heat absorption or production within the material at a given time. The crystallization model was replaced with a thermoset cure model. The results of this model were verified with test cases that could be solved by analytical means.

Dave et al. [47] developed a more sophisticated void model and combined it with previous thermal modeling techniques for autoclave consolidated composites. The void model was then verified, tested, and used to make generalizations about the effects on polymer cure and void formation in autoclave cured composites that are dependent on the initial condition of the material.

An interesting approach to the modeling of thermoset matrix composite manufacture was developed by Pitchumani and Yao [48]. The model used an idealized non-dimensional approach for the heat transfer and the kinetics of the chemical reaction occurring during the production process. The goal of this approach was to generalize a cure model for the production of thermosetting composites such that the analysis would be independent of the selected material system or the geometry of the manufacturing
process. The resulting effect is a reduction in the number of process parameters. A simplified case was given to illustrate the models ability to predict optimum cure cycles.

The conclusions obtained from the formulation of these models reveal some of the important material considerations that must be made for the Curved LOM process. Foremost among these in this analysis, it is clear that the thermal phenomena occurring within the part affects other important phenomena such as resin flow, cure, and void formation. Relationships between all of these effects have been characterized in thermosetting composites as has been described. The thermal phenomena in the Curved LOM process are different from autoclave processing only in that the Curved LOM process is both additive and cyclic in nature. Thus, one can still apply concepts relating to the individual phenomena (e.g. thermal effects on viscosity, pressure effects on voids) to this process. However, the cyclic nature of the Curved LOM process itself requires a reexamination of the means by which temperature predictions are made within the part. Therefore, it is necessary to make an assessment of the process and develop a model that more realistically represents the process and will more readily predict the thermal phenomena that occurs.
CHAPTER III
MODEL DEVELOPMENT

This chapter describes the assumptions and underlying principles that define the mathematical model for the Curved LOM process. The solution method is also discussed in detail.

3.1 Curved LOM Heat Conduction Model

The models that have been developed for the standard LOM process are lacking two critical elements associated with Curved LOM and the manufacture of advanced materials. First, the method of lamination via the Curved LOM process is different than that of the standard LOM process. A heated roller applies heat to the part block in the standard LOM process while the Curved LOM process adds heat via a conformable heated pad. Secondly, certain advanced materials produce heat during lamination. For example, uncured thermosetting composites produce heat at elevated temperatures due to the exothermic curing reaction. This exothermic reaction is significant and should be accounted for in a model that would predict temperatures in thermosetting laminates. Therefore, an accurate model of the Curved LOM process must account for both of these heat transfer aspects.

The rationale for developing a mathematical model of Curved LOM is based on the cyclic thermal environment encountered in the layer-by-layer lamination process. For chemical and physical processes occurring in advanced materials, such as the cure of a
thermoset resin or crystallization of a thermoplastic polymer, the thermal history of the
part plays a key role in determining the mechanical properties of the final parts.
Predicting thermal fluctuations in the LOM process is not a straightforward process. The
effects of the cyclic laminator heating and chamber temperature must be accounted for in
such predictions. In addition, the process also involves the layer-by-layer addition of
material. As a result, previous models of composite cure cycles (i.e. batch processes)
would not be applicable in this case. A separate mathematical model must be developed
to deal with the varying heat effects that occur during the LOM process.

The basis for the Curved LOM model was taken from a model previously
developed at the University of Dayton for the standard LOM process [15, 16]. The
thermal behavior of a LOM part is primarily determined by the heat transfer mechanisms
that take place during the LOM build cycle. These mechanisms include heat transfer from
the heated laminator to the surface of the partially completed part, heat conduction within
the part itself, heat production within the part due to chemical reaction, heat loss from the
bottom of the part to the paper mandrel and the metal base-plate on which the part is being
fabricated, and heat loss from the various exposed surfaces of the part to the surroundings
via free or forced convection. These heat transfer mechanisms determine the temperature
profiles that develop in the LOM part during the various phases of the build cycle, thus the
mathematical model developed must describe them as accurately as possible.

The mathematical model was developed for a simple rectangular geometry LOM
part. This allows for the use of the Cartesian coordinate system. The geometry for the
analysis is shown in Figure 4. This figure also illustrates the experimental setup for the
verification procedure, described in the next chapter. Points T0, T4, T8, T12, and T16
represent the locations where the model will report temperature predictions. The difficulties in modeling a curved geometry were not addressed in this model. To account for the curvature, it is thought that existing geometric transformation techniques [49] could be applied once a workable model for rectangular geometry is developed. Finite element modeling could also be applied. To further simplify the analysis, heat transfer from the sides of the part was ignored. This assumption, which is valid for the thin panels that are typically fabricated on the Curved LOM machine, reduced the problem to a transient, one-dimensional heat transfer problem. The assumption further validates the use of rectilinear coordinates and this model’s applicability of a curved geometry as well. For thin panels with curvature, the difference in the length of the top and bottom surfaces is negligible. Also, the thermal properties of the material (density, thermal conductivity, and heat capacity) are assumed to be independent of the temperature in the analysis. This further simplifies the analysis and is a standard assumption in most heat transfer models.

![Diagram](image)

**Figure 4:** Model geometry and experimental set-up (not to scale).
Heat conduction within the rectangular region of material is described by the equation of energy [50] and is simplified to the following form:

\[ \rho C_p \frac{\partial T}{\partial t} = \nabla \cdot (k \nabla T) + \rho R_p \Delta H_p \quad (3) \]

The source term that is included in this model is the rate of heat production within the material of construction due to chemical reaction. This consists of the total heat of reaction per unit mass (\( \Delta H_p \)) and the rate of reaction (\( R_p \)). This rate of reaction is given by a thermoset cure model, which is a direct kinetic relationship between the degree of conversion and time. To maintain unit consistency, it is necessary to multiply the rate by the mass density (\( \rho \)). While polymer flow is expected to occur in the material of construction, heat production due to viscous dissipation is assumed to be negligible and is ignored.

Boundary conditions for the part are specified using general heat transfer coefficient boundary conditions. This type of boundary condition is used often to approximate convection heat transfer from a solid body to a fluid. When the top part surface is in contact with the surrounding air, the following expression applies:

\[ k_z \frac{\partial T}{\partial z} = h_{air} (T_{surface} - T_{air}) \]

The value of the heat transfer coefficient (\( h_{air} \)) selected should be appropriate for the airflow regime around the part being fabricated (i.e., free convection or forced convection).

The heat transfer coefficient boundary condition was also selected to approximate the imperfect thermal contact between the part and the laminator as well between the part and the LOM-paper mandrel. For times when the top surface is in contact with the laminator, a similar expression was used:
\[
k_z \frac{\partial T}{\partial z} = h_{lam}(T_{surface} - T_{lam})
\]

The use of this approach to describe the limited heat transfer that occurs from the laminator to the part was successfully used in a similar model [15, 16]. This approach is simple and allows for experimental tuning of the model to actual lamination conditions, which are inherently difficult to model. The part fabricated by the Curved LOM process is supported by a solid mandrel. In this study, the boundary between the part and the paper mandrel (block) is also accommodated using a heat transfer coefficient boundary condition as follows:

\[
k_z \frac{\partial T}{\partial z} = h_{base}(T_{bottom} - T_{base})
\]

where \( T_{bottom} \) in the temperature at point T0 in Figure 4. The base plate temperature \( T_{base} \) is treated as a single parameter that is approximately equal to room temperature in practice. The heat transfer coefficient for the paper block \( h_{base} \) is an effective value that can be estimated or experimentally measured. This approach for estimating the heat flow from the bottom of the part through the paper mandrel to the aluminum base plate (which acts as a heat sink) eliminates the complexity of having to include heat conduction within the LOM-paper mandrel to the Curved LOM model. This modeling approach was also used with success previously [15, 16] although the element between the LOM part and the aluminum base plate was much thinner. To investigate what effect this might have, the use of both a heat transfer coefficient and a conductive approach to modeling the LOM-paper base is considered in this study.
3.2 Curved LOM Model Solution Approach

The simulated processing cycle for each layer consisted of three phases: new layer placement on the existing stack, layer lamination, and layer cooling during laser cutting. Heat input by laser cutting was not considered, since it was observed in practice to have a negligible impact on the overall body part temperature. To determine the temperature distribution of the part throughout the experiment, a scheme for representing the layers of material had to be devised. To accomplish this, a one-dimensional, equally spaced position grid was generated as shown in Figure 5. This scheme was selected because it facilitates use of the solution technique, which is described in the following paragraphs. Also, there appeared to be no rationale to favor a higher grid spacing in any one region over another region. Each node of the grid represents the top, center or bottom of a layer. Addition of a new layer of material was accomplished by adding an additional pair of nodes to the existing spatial grid structure. Thus the grid grows throughout the simulation.

Finite difference approximations were applied to the derivatives in the heat conduction equation and the boundary conditions. Specifically, central difference approximations were applied to the partial derivatives with respect to position and a forward difference approximation was applied for the partial time derivative. The equations were combined in a manner that allows for a solution based on the initial conditions of the experiment. These conditions include the initial temperatures of the material, the surrounding air, and the base plate. Applying the finite grid to the equations results in a set of linear equations for each time increment and a one-dimensional spatial grid, which grows in size as layers are added at discrete times. The coefficients of the
temperature variables were calculated and the equation set is solved using a Thomas Method algorithm described by Carnahan, Luther, and Wilkes [51]. It was assumed that each new layer of material was at ambient temperature. The temperature discontinuity at the instant of new layer application was handled by simply adjusting the temperature of the interfacial node to the average of the previous layer’s surface temperature and the temperature of the new layer.

![Figure 5: Selected Position Grid for Curved LOM Model Solution](image)

The reaction rate equation must be solved simultaneously with the heat conduction equation so that the cure distribution can be estimated. The reaction rate determines the amount of heat that is produced in any given time increment. However, this reaction rate is temperature dependent. To simplify the calculations and to minimize memory usage and calculation time, it is assumed that the reaction rate for a given time increment at a specified grid node can be determined from the temperature that was
calculated at that position in the previous time increment (i.e., $T_z, t^{-\Delta t}$). This assumption can produce substantial errors if the temperature change at a given spatial position is adequately high. However, it is believed that a sufficiently small time increment in the calculations can offset such errors. Using this assumption, the cure rate can be estimated directly, and the cure distribution is determined numerically by using a modified Euler predictor-corrector technique. [51]

The solution technique described above was coded into a FORTRAN language program that determines the temperature and cure distribution throughout the parts (see Appendix B). Output from the model is reported from locations $T_0$, $T_4$, $T_8$, $T_{12}$, and $T_{16}$ as marked in Figure 4. The temperature predictions can then be compared to experimentally measured values produced from the experimental build from a given material of construction with thermocouples embedded at the specified locations.
CHAPTER IV

EXPERIMENTAL APPROACH

This chapter details the experimental procedures used to determine the various parameters and material properties required by the Curved LOM process model. Also described is the experimental procedure used to verify the model itself.

4.1 Experimental Verification of Curved LOM Model

4.1.1 Verification Approach

A simple experiment was conducted with two different material systems to verify the model performance. A twenty-layer part was built using an off-line, physically simulated Curved LOM building process. A spare aluminum base plate from a LOM 2030 machine was placed on a tabletop. The same type of base plate is used in the Curved LOM machine. A 10-cm x 10-cm x 1.25-cm LOM-paper block was placed on the aluminum plate and acted as the mandrel upon which the part was built. This block was previously fabricated on a LOM 2030 machine using Helisys LPH0042 LOM-paper. A simple laminator was fabricated consisting of a flexible, 25-cm x 25-cm, 500 W heating pad placed between two 1.5-mm thick pieces of rigid aluminum sheet. The temperature of the pad was controlled using an Omega PI controller via a thin thermocouple sandwiched between the heater pad and the supporting aluminum sheet.

The lamination procedure consisted of manual placement of the 10-cm x 10-cm sheets of build material on the LOM-paper block followed by a release ply (Mylar film or
non-porous Teflon™ sheet) to prevent the material from sticking to the sheet metal surface. Then, the heater assembly was manually placed on the build stack, and an insulated 6.1-kg weight was placed on top of the heater. The resulting pressure was 6 kPa (~1 psi), which was sufficient to produce good thermal contact between the laminator and the part.

A twenty-layer, 10 cm x 10 cm rectangular block of the build material was fabricated atop the LOM-paper block using the sequence given in Table 2. This cycle realistically represents the cycle previously described for the Curved LOM process (Figure 2). A thin (0.075 mm diameter) thermocouple was placed in the center of the top surface of every fourth layer beginning with layer 0 (the top of the paper mandrel). A thermocouple was also placed below the paper mandrel to verify that the temperature between the base plate and the mandrel remained steady. The temperature from each thermocouple was recorded every 0.5 seconds through the entire 30-minute build using a computer data acquisition system. This system and thermocouples attached to it were previously calibrated at 0°C and 100°C. Experimental temperature profiles were subsequently compared to model predictions.

Table 2: Curved LOM process sequence.

<table>
<thead>
<tr>
<th>Process Step</th>
<th>Action</th>
<th>Duration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Layer Placement</td>
<td>Place new material layer on top of stack</td>
<td>10 seconds</td>
</tr>
<tr>
<td>Layer Lamination</td>
<td>Quickly place film on top of stack; quickly place heater and weight; wait</td>
<td>40 seconds</td>
</tr>
<tr>
<td>Laser Cutting/ Cool Down</td>
<td>Quickly remove weight, heater, and film; wait (no attempt was made to add heat to simulate laser cutting)</td>
<td>40 seconds</td>
</tr>
</tbody>
</table>
4.1.2 Description of Materials for Verification

Two materials were selected to verify the Curved LOM heat transfer model during various stages of development. To verify and tune the heat conduction portion of the model (i.e., prior to the implementation of the heat generation sub-model), a non-reactive material was selected. When this part of the model was satisfactorily verified, a thermosetting polymer composite material was used to verify the complete Curved LOM model.

The non-reactive material that was selected to verify the heat conduction portion of the model was a monolithic silicon carbide (SiC) ceramic tape cast by Lone Peak Engineering [52]. The tape contains SiC powder supplied by the Jerico Company [53]. Ceramic tapes were comprised of SiC particles embedded in a highly plasticized thermoplastic polymer [2]. The overall composition of the material by weight was approximately 65% SiC powder (coarse and fine particles), 25% binder system (thermoplastic binder and plasticizer), and 10% carbon and graphite powders. In a previous study, this material was used to verify the heat transfer model developed for the standard LOM process [15, 16]. The material does not undergo an endothermic (e.g., melting) or exothermic process in the temperature range to be investigated. This allowed for selective verification of the heat conduction portion of the Curved LOM model.

To verify the complete Curved LOM thermal model for the process, which includes a heat generation/ cure sub-model, a thermoset polymer prepreg number 95-147, supplied by Lectromat, Inc. [53], was selected for the process. The prepreg consisted of a woven E-glass fiber mat impregnated with a B-staged catalyzed Novolac epoxy resin system. The glass fiber cloth was a plain weave style 7628. The resin content of the
prepreg was reported to be approximately 35 percent. The average thickness of the prepreg was measured as 0.0085 inches. The material was supplied on 12-inch rolls and had a shelf life of 3 months at room temperature. The material was stored at 0°C and had an approximate shelf life at this temperature of 6 months [55]. It was believed that despite the B-staging of the resin, there was a sufficient amount of cure remaining in the polymer that it could be used to demonstrate the effects of a material’s heat production during the Curved LOM process.

To prepare materials for the 20-layer verification trials, 4-inch square layers of the ceramic tape and the prepreg were cut from larger sheets using a razor blade. The length and width reported are nominal values correct to within 1 mm. Layer thickness was measured with a micrometer.

4.2 Selection and Determination of Cure Model Parameters

The usefulness of the Curved LOM model will ultimately depend on its versatility. A generalized sub-model describing the cure kinetics of a thermosetting material is needed. Keeping this in mind, the selected cure model should not only accurately represent the material to be used on the Curved LOM process, but it should also be modular so that more than one cure model type can be entered into the overall Curved LOM model. The model should also be able to operate in the full cure regime (i.e., estimate degree of cure and cure rate during the entire cure process). The kinetic rate expression that was selected for the Curved LOM model was:

\[
\frac{d\alpha}{dt} = \left( k_1 + k_2\alpha^m \right) (1-\alpha)^n
\]  

(3)
where \( \alpha \) is the degree of cure, \( m \) and \( n \) are the reaction order exponents, and \( k_1 \) and \( k_2 \) are rate constants. This model has the ability to model nth-order and autocatalytic kinetic cure reactions. The use of this equation to model autocatalytic cure equations has been well-established [36]. Ryan and Dutta [56] provide a simplified method for determining the parameters of the model for autocatalytic reactions from Differential Scanning Calorimetry (DSC) data. The data manipulation process prescribed by Ryan and Dutta is explained in Appendix C. However, a description of the experimental method that was used in this study follows.

Cure of the glass/epoxy prepreg was monitored with a DuPont Instruments 2910 Differential Scanning Calorimeter with a DSC cell supplied by TA Instruments [57]. The operation and principles of this instrument are discussed in other theses [4, 58] as well as the operation manual [59]. To summarize the process, a sample of a given material is placed in a sealed aluminum pan. The heat flow to this sample is compared to an empty reference pan. Measurements can be made isothermally or with a linear temperature ramp. The differential heat flow measurements made by DSC can provide information on the thermal characteristics of certain materials. Most often, it is used to determine the locations of thermal transitions in polymers and other materials.

First, it was necessary to obtain the overall heat of reaction for the material. This value was necessary to determine the degree of cure and the cure rate. To obtain this value, a dynamic DSC scan was performed on the material at a rate of 10°C per minute.
The TA Instruments thermal analysis software was used to integrate the heat flow data to calculate the heat of reaction.

Generally speaking, DSC is unable to directly monitor the degree of cure of a given sample. However, equations to relate the heat flow measurements to the degree of cure are established and widely used. The following relations relate the cure rate and the degree of cure to isothermal heat flow measurements:

\[
\left( \frac{d\alpha}{dt} \right)_{t=t_a} = \frac{dH}{dt} \bigg|_{t=t_a} \frac{1}{\Delta H_p}
\]

(6)

\[
(\alpha)_{t=t_a} = \int_0^t \frac{(dH/dt)}{\Delta H_p} dt
\]

(7)

Isothermal DSC scans were performed on the prepreg at four temperatures: 105, 110, 115, and 120°C. The DSC heat flow, \((dH/dt)\), was measured as a function of time. A thermal analysis program developed by TA Instruments performed the numerical integration on the isothermal heat flow data. The total heat of reaction was provided by the dynamic DSC scan. Upon manipulation of the heat flow data to obtain the cure rate and the degree of cure, the equations given in Appendix C were applied to obtain the activation energies, pre-exponential factors, and reaction order exponents \(m\) and \(n\) as given in equations 3-5.

4.3 Thermal Property Determination

The developed thermal model requires that several material properties and process conditions be measured or otherwise determined. The material thermal properties that are needed are the density, heat capacity, and thermal conductivity. The other properties that
are needed are the various heat transfer coefficients and the initial temperature conditions. The initial temperatures are measured at the beginning of the experiment by thermocouples. Two of the three necessary heat transfer coefficients were determined in a previous study [60] using the SiC tapes. The value measured for air convection is 13.6 Wm\(^{-2}\)K\(^{-1}\). The value of the heat transfer coefficient at the bottom of the stack (based on the cooling curve analysis prescribed in [60]) was estimated at 8.5 Wm\(^{-2}\)K\(^{-1}\). It is assumed that the same measured values hold for the prepreg.

Strong [58] and Klosterman et al. [60] previously determined the properties of the monolithic silicon carbide tapes. In the current study, the same procedures were followed to determine of the bulk density and heat capacity of the polymer prepreg. The thermal conductivity of the prepreg cannot be determined by the method prescribed by Strong because the method has an implicit assumption of no heat production within the part. The thermal conductivities of glass fiber preforms and epoxy resins are well established in the literature [61]. The value used for thermal conductivity of the prepreg in the model was estimated from median values of the thermal conductivity for E-glass fiber (10.4 Wm\(^{-1}\)K\(^{-1}\)) and amine cured epoxy resins (0.20 Wm\(^{-1}\)K\(^{-1}\)). A volume weighted average of the thermal conductivities of the glass fiber and resin produced the value that would be used in the model as follows.

\[
\frac{1}{k^{(p)}} = \frac{V_f^{(g)}}{k^{(g)}} + \frac{V_f^{(e)}}{k^{(e)}}
\]  

(8)

where superscripts p, g and e refer to the prepreg, E-glass, and epoxy resin respectively. The ultimate thermal conductivity value was calculated to be 0.31 Wm\(^{-2}\)K\(^{-1}\).
CHAPTER V

RESULTS AND DISCUSSION

This chapter details the results of the experiments used to verify the Curved-LOM model. Included are measurements of material properties and chemical reaction kinetics of epoxy cure, which are all necessary as model inputs. The developed model was verified with results of an analytical heat transfer result and two separate Curved LOM builds, each of which used a different material. A SiC ceramic tape was used to verify the heat transfer portion of the model. The glass fiber/epoxy matrix prepreg was used to verify the complete Curved LOM model, including the source heat model and the cure model.

5.1 Material Properties

The properties of the materials used in the verification process are necessary inputs to the heat transfer portion of model. These properties have been previously determined [15, 58, 60] for the ceramic tapes and are listed in Table 3. The properties of the glass/epoxy prepreg were determined by the same methods, as described next.

Determination of the bulk density was calculated from an average of three measurements of data. The results are outlined in Table 4. The analysis was performed on two 20-layer samples and a 3-layer sample. The actual 20-layer blocks fabricated during the Curved LOM process experimental runs (as described in section 4.1.1) were used for the density measurements. The 3-layer part was then laminated by the same
process. The average of these measurements was used in the model for the final Curved LOM simulation. The average value for the bulk density was determined to be 1.70 g cm\(^{-3}\).

**Table 3:** Thermal Data for Curved LOM build simulation for SiC tapes

<table>
<thead>
<tr>
<th>Material</th>
<th>SiC tapes</th>
<th>Glass/epoxy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal Conductivity, (k_x)</td>
<td>1.25 Wm(^{-1})K(^{-1})</td>
<td>0.31 Wm(^{-1})K(^{-1})</td>
</tr>
<tr>
<td>Density, (\rho)</td>
<td>1.98 g cm(^{-3})</td>
<td>1.70 g cm(^{-3})</td>
</tr>
<tr>
<td>Heat Capacity, (C_p)</td>
<td>1.05 Jg(^{-1})K(^{-1})</td>
<td>1.39 Jg(^{-1})K(^{-1})</td>
</tr>
<tr>
<td>Layer thickness</td>
<td>0.33 mm</td>
<td>0.22 mm</td>
</tr>
<tr>
<td>Number of layers</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>Heat transfer coefficient (part to air), (h_{air})</td>
<td>13.6 Wm(^{-2})K(^{-1})</td>
<td></td>
</tr>
<tr>
<td>Heat transfer coefficient (part to base), (h_{base})</td>
<td>8.5 Wm(^{-2})K(^{-1})</td>
<td></td>
</tr>
<tr>
<td>Air temperature, (T_{air})</td>
<td>23°C</td>
<td>16°C</td>
</tr>
<tr>
<td>Base plate temperature, (T_{base})</td>
<td>25°C</td>
<td>16°C</td>
</tr>
<tr>
<td>Initial temperature of material</td>
<td>23°C</td>
<td>16°C</td>
</tr>
<tr>
<td>Laminator temperature, (T_{lam})</td>
<td>110°C</td>
<td>130°C</td>
</tr>
<tr>
<td>Build cycle time</td>
<td>90 seconds</td>
<td></td>
</tr>
</tbody>
</table>

**Table 4:** Bulk density determination data for the glass/epoxy prepreg

<table>
<thead>
<tr>
<th>Sample</th>
<th>Length (cm)</th>
<th>Width (cm)</th>
<th>Thickness (cm)</th>
<th>Mass (g)</th>
<th>Density (g/cm(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10.16</td>
<td>10.16</td>
<td>0.383</td>
<td>65.71</td>
<td>1.662</td>
</tr>
<tr>
<td>2</td>
<td>10.16</td>
<td>10.16</td>
<td>0.371</td>
<td>66.48</td>
<td>1.736</td>
</tr>
<tr>
<td>3</td>
<td>10.16</td>
<td>10.16</td>
<td>0.057</td>
<td>10.09</td>
<td>1.715</td>
</tr>
</tbody>
</table>

**Average =** 1.704

Results of the heat capacity analysis are shown in Figure 6. A dynamic DSC scan was performed at a rate of 10°C per minute between baseline isothermal holds at 30°C and 300°C. The TA Instruments thermal analysis software performed the calculations. The analysis was performed on an uncured sample of the prepreg. The exothermic reaction peak was excluded from the analysis and replaced with a linear interpolation of the data. An examination of the results reveals that the heat capacity of the completely cured prepreg (approximately 0.95 Jg\(^{-1}\)K\(^{-1}\)) is different than the heat capacity of the
Figure 6: DSC heat capacity analysis on uncured prepreg sample. The centrally marked region represents the region of excluded exothermic peak.

Figure 7: DSC heat capacity analysis on completely cured prepreg sample.
uncured sample (approximately 1.4 Jg⁻¹K⁻¹). This was verified by a heat capacity
analysis on a completely cured sample (Figure 7). Thus, the value that was selected for
the uncured material was that at 90°C, a temperature prior to the reaction exotherm. This
value, 1.39 Jg⁻¹K⁻¹, was selected because it is a median value and it falls in the center of
the temperature range that will be applied in the verification of the model. These results
clearly show that the assumption of constant thermal properties is invalid for this
material; nonetheless, it is hoped that model results will not be sensitive to this
assumption.

5.2 Cure Sub-Model Analysis

The first parameter to be determined in the kinetic cure sub-model was the
exothermic heat of reaction for the glass/epoxy prepreg. This required the measurement
of the heat release from a sample of the prepreg through the complete progress of the
reaction. Five separate dynamic DSC scans were performed at a rate of 10°C per minute
on prepreg samples that were randomly taken from various locations on the prepreg roll.
The heat of reaction was determined by dynamic DSC to be 106.5 ±3.8 Jg⁻¹. A typical
DSC result is shown in Figure 8. Note that the value is normalized with the mass of the
prepreg. Given that the prepreg is approximately 35% resin by weight [55], the true heat
of reaction produced by the neat epoxy resin was approximated to be 304 Jg⁻¹, which is a
typical value for epoxy resins. However, since all experiments performed herein involve
the prepreg, the value obtained for the entire prepreg material is relevant. Repeatability of
the DSC dynamic 10°C per minute scan was excellent. The measured values in each scan
ranged from 101 Jg⁻¹ to 109 Jg⁻¹. The temperature difference between the reaction onset
temperature and the reaction completion temperature was approximately 50°C in each scan.

Figure 8: Typical DSC scan and heat evolution analysis.

To determine the values of the cure model kinetic parameters, single isothermal DSC scans of the glass/epoxy prepreg were performed at four temperatures: 105°C, 110°C, 115°C, and 120°C. These values were selected because they are within the range recommended by the program that performs the kinetic analysis. Using the Isothermal Kinetics program by TA Instruments [57], the DSC data were appropriately integrated so as to determine the heat of reaction, reaction rate and the degree of conversion for each time measurement. Using the equations developed by Ryan and Dutta (Appendix C and [56]), which require the assumption of an overall second order process (a common assumption for the kinetic modeling of epoxy resins [36]), the values of the activation energies, pre-exponential factors, and exponents are calculated and listed in Table 5. The
semi-log plots used to determine the activation energy and pre-exponential factors are shown in Figures 9 and 10. The collected rate constant data sets fit the Arrhenius expression very well. The equations from Appendix C were used to calculate the values of the exponents.

Table 5: Kinetic parameters determined for glass/epoxy prepreg.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta H_p$ (J/g)</td>
<td>106.5</td>
</tr>
<tr>
<td>$m$</td>
<td>0.691</td>
</tr>
<tr>
<td>$n$</td>
<td>1.309</td>
</tr>
<tr>
<td>$E_1$ (J/mol)</td>
<td>-67536.5</td>
</tr>
<tr>
<td>$A_1$</td>
<td>1.49E+07</td>
</tr>
<tr>
<td>$E_2$ (J/mol)</td>
<td>-70263</td>
</tr>
<tr>
<td>$A_2$</td>
<td>3.74E+08</td>
</tr>
</tbody>
</table>

Figure 9: Activation energy and pre-exponential factor determination for rate constant 1 ($k_1$) given in units of min$^{-1}$. 
Figure 10: Activation energy and pre-exponential factor determination for rate constant 2 ($k_2$) given in units of min$^{-1}$.

Figure 11: Comparison of Cure Model rate predictions to DSC kinetic measurements.
Using the values from Table 5, the model's results were compared to the isothermal DSC analysis. These results, shown in Figure 11, show the actual data calculated from the DSC Isothermal Kinetics Program against the values predicted by the model. The general profile of the model predictions follows the contour of the actual data, but some degree of error can be seen in the results, especially near the beginning of the reaction. However, previous works on cure modeling suggest that minor cure rate inaccuracies can be insignificant in the determination of other properties, such as in-situ temperature and viscosity [40].

**Figure 12:** DSC scan of polymer prepreg aged to estimated degree of cure of 0.50. (18.59 min. at 110°C)

To initially verify the cure model, a half-life experiment was performed on a sample of the prepreg. The calculated half-life value obtained from the model at 110°C was 18.59 minutes. Thus a DSC scan of the prepreg was executed consisting of an
isothermal hold at 110°C for 18.59 minutes, followed by an immediate quenching with liquid nitrogen and a dynamic scan at 10°C per minute. The dynamic portion (i.e. dynamic scan) of the experiment is shown in Figure 12. The heat evolution was measured from the dynamic DSC scan to estimate the amount of cure that had taken place during the hold. The value obtained from the scan is 56.3 Jg⁻¹, equating to a degree of cure equal to 0.471. Based on the relative error in the heat measurements with DSC in general, this error was deemed acceptable relative to the expected value of 0.5. Therefore, this cure sub-model should be sufficiently accurate to used in the Curved LOM model.

5.3 Verification of Heat Transfer Model

5.3.1 Analytical Heat Transfer Comparison

To initially verify the Curved LOM model without the cure sub-model, the results of the model were compared to an analytical solution for one-dimensional heat transfer in a solid slab of finite thickness. The solution, developed by Carslaw and Jaeger [62], calculates values for the dimensionless temperature given values for dimensionless time, dimensionless thickness, and thermal diffusivity. The equation derived from the general solution is:

\[ \theta = \eta + \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{(-1)^n}{n} \exp(-n^2 \pi^2 \tau) \sin(n\pi\eta) \]

(9)

where \( \theta \) is the dimensionless temperature, \( \tau \) is the dimensionless time, and \( \eta \) is the dimensionless thickness. These dimensionless quantities are related to the actual desired quantities by the following relationships:
\[
\theta = \frac{T - T_0}{T_1 - T_0} \\
\tau = \frac{at}{b^2} \\
\eta = \frac{z}{b}
\]

(10,11,12)

where \(T_0\) and \(T_1\) are temperatures on the lower and upper faces of the slab respectively, \(b\) is the slab thickness, \(t\) is the elapsed time since the temperature conditions were applied and \(z\) is the variable distance from the lower slab face. The thermal diffusivity of the silicon carbide tape was used for the sake of this analysis as it was the verification material of choice in this and previous modeling studies [15, 16]. Even so, any value can be used as long as the same value is used in the analytical model above and in the Curved LOM model.

Several adjustments had to be made to the Curved LOM model for the sake of comparison to the analytical solution. The analytical solution to the heat transfer equation that was developed by Carslaw and Jaeger [62] assumes a constant temperature at the boundaries of the solid. Since the boundary conditions in the Curved LOM model are of the convective type, the heat transfer coefficients had to be sufficiently large so as to force the temperature at the top and bottom surfaces to remain relatively constant at \(T_0\) and \(T_1\). The value for the heat transfer coefficient that was used for this comparison on both the top and bottom boundaries was \(10^9\) Wm\(^{-1}\)K\(^{-1}\). Secondly, the LOM model was modified to handle dimensionless variables for a singular layer of thickness \(b\). These allowed for direct comparison of the Curved LOM model with analytically determined results.
The results of the comparison between analytical and model-generated values are shown in Figure 13. The graph represents the prediction of temperature from a single lamination step using the Curved LOM model and the analytical solution for the geometry of the problem. This comparison shows that predictions made by the model are sufficiently close as to verify that the calculations made by the model fall in line with theoretical heat transfer results. This analysis also helps to connect the results of thermal observations of the LOM process to theoretical predictions for heat transfer in such a realm.

5.3.2 LOM Build Verification of Heat Conduction Model

The heat conduction model was more fully verified with a physical simulation of a Curved LOM lay-up with the non-reactive, monolithic silicon carbide (SiC) tape. The experimental results of the physical Curved LOM build are shown in Figure 14. In this
figure, the temperatures were measured from thermocouples embedded under the first layer (T0), over the eighth layer (T8), and over the sixteen layer (T16), as is marked in Figure 4. Figure 15 shows the temperature recorded by thermocouple T8 during the lamination of four layers immediately above it. The general thermal characteristics that are expected of the cyclic process exhibit themselves in the results. In Figure 15, the three stages of the Curved LOM cycle are highlighted. The layer lamination step is accompanied by an inverse exponential rise in temperature. The subsequent exponential of the part occurs via conduction through the mandrel and base plate, and by convection to the surrounding air. Finally, a sharp drop in temperature occurs when a new layer is placed on top of the stack.

![Temperature Profiles](image)

**Figure 14:** In-situ, experimental temperature profiles for 20-layer monolithic SiC block laminated with Curved LOM process.
Model predictions for the system were made using the data given in Table 3. The only parameter not given in this table and not known before the experiment was the heat transfer coefficient for the heat transfer from the laminator to the part top (h_{lam}). The most noticeable effect of adjusting this heat transfer coefficient in the model was the difference in the ultimate part temperature. Thus the value was adjusted until the model predicted the steady state temperature achieved in the experiment (~90°C). The result, in which h_{lam} is set at 275 Wm^{-2}K^{-1}, is shown in Figure 16. In comparing the data, a reasonable match of the steady state response was obtained. However, as can be seen in Figure 17, this heat transfer coefficient value resulted in an over-prediction in the temperature rise in the initial layers. Yet, the predictions for other thermocouples and at later times in the process are much better (see Figures 17, 18, and 19).
These results suggest that one of the heat transfer coefficients changes as the LOM build progresses, or that fluctuations in the temperature of the laminator have a profound effect on the results of the experiment. One possible hypothesis is that the base heat transfer coefficient changes during the build. The possible cause of this phenomenon is the temperature increase in the LOM-paper mandrel, which affects the heat transfer dynamics. The heat transfer coefficient boundary condition at the bottom of the stack is suspected as the problem because it cannot be expected to fully represent what is essentially a conductive (and therefore more complex) condition. For example, heat up of the LOM-paper block is rapid at the beginning of the experiment, which would indicate that the heat transfer coefficient applied to represent this boundary might change radically at the beginning as well.

Figure 16: Model results for 20-layer monolithic SiC block using $h_{\text{lam}} = 275 \text{ W/m}^2\text{K}$. 
Figure 17: Comparison of model to experimental data for thermocouple #0 (T0) embedded in 20-layer SiC block, using $h_{\text{am}} = 275 \text{ W/m}^2\text{K}$.

Figure 18: Comparison of model to experimental data for thermocouple #8 (T8) embedded in 20-layer SiC block, using $h_{\text{am}} = 275 \text{ W/m}^2\text{K}$.
Figure 19: Comparison of model to experimental data for thermocouple #16 (T16) embedded in 20-layer SiC block, using $h_{\text{lam}} = 275 \, \text{W/m}^2\text{K}$.

To compensate for the heat transfer dynamics that occur in the LOM-paper mandrel, the thermal model was adjusted to accommodate heat conduction between two materials. This modification would allow prediction of the temperature distribution within the SiC block as well as throughout the LOM-paper block. An inherent assumption made in the model adjustment was that there was perfect thermal contact between the ceramic tape and the LOM-paper block, meaning that there is no interfacial resistance to heat transfer included in the model. The results of this adjusted model are shown in Figure 20. The same phenomenon of temperature over-prediction in the initial layers is observed with this model as well, but certain characteristics improve in the prediction. For example, the thermal gradient that is predicted from layer to layer is larger than in the previous prediction; therefore, it better represents the experimental
temperature distribution in this respect. However, the actual magnitudes of temperature prediction are less accurate. Thus, this strategy did not achieve the previously stated goal.

The temperature comparison of the adjusted model to the experimental data is given in Figure 21. The fit in this case is not as good at long times as with the previous case. This cause of the error is the assumption of a thin part. This assumption allowed the use of one-dimensional equations in the model to predict the temperature distribution. In the model developed without heat conduction in the mandrel, less than 2% of the heat transfer area is ignored in the analysis because the SiC block is thin. However, this model does not account for 35% of the heat transfer area due to the thickness of the LOM-paper.

![Graph showing temperature vs. time](image)

**Figure 20:** Results of the Curved LOM model adjusted to include heat conduction in the LOM-paper base ($h_{\text{lam}} = 375 \text{ W/m}^2\text{K}$), predicting temperature in the 20-layer SiC block.
Figure 21: Comparison of adjusted model to experimental data for thermocouple #8 (T8) embedded in 20-layer SiC block, using $h_{\text{lam}} = 375$ W/m$^2$K.

block. This effect will lead to substantial error, especially at long times as observed. Thus, the initial model (without heat conduction within the LOM-paper mandrel) will become the basis for the final, complete, mathematical model for the Curved LOM process.

5.3.3 Verification of Complete Curved LOM Model

The complete Curved LOM model was verified with experimental temperature profiles from a physical simulation of Curved LOM manufacture with the thermoset polymer prepreg. The same physical process configuration and sequence were used in the simulation as with the SiC ceramic tapes. The lamination temperature was modified to ensure that cure of the prepreg material would contribute to the heat transfer in the experiment. The parameters of the simulation are shown in Table 3 for the thermal
properties and Table 5 for the kinetic parameters. As was the case for the previous physical verification, the build consisted of a twenty-layer, 10 cm x 10 cm, flat rectangular laminate. The simulation was performed with a laminator temperature of 130°C.

The experimental results of the Curved LOM build with the polymer prepreg are shown in Figure 22. Again, the temperatures in this figure were measured from thermocouples embedded under the first layer (T0), over the eighth layer (T8), and over the sixteenth layer (T16), as is marked in Figure 4. The observed response is similar to the response observed for the ceramic tapes. The three stages of the Curved LOM process are apparent.

The temperatures simulated by the complete Curved LOM model are shown in Figure 23. A laminator-to-part heat transfer coefficient of 275 Wm⁻²K⁻¹ again results in the best match of the model to experimental data. This quantitative result appears to validate the practice of using a heat transfer coefficient boundary condition to describe the lamination heat input as well as the value itself. The nature of the response matches the experimental data. Also, quantitative agreement is apparent as the process continues to proceed, as is shown for thermocouples T0, T8, and T16 in Figures 24, 25, and 26 respectively. Figure 27 shows an enlargement of the comparison of the data sets for thermocouple #8 at layer 9. This figure more clearly illustrates the similarities between the model and the experiment. The overall shape of the curve is approximated very well, indicating that the model is able to accurately simulate the temperature distribution throughout the process.
Figure 22: In-situ, experimental temperature profiles for 20-layer glass/epoxy prepreg part laminated with the Curved LOM process.

Figure 23: Curved LOM simulation results for 20-layer glass/epoxy part, using $h_{\text{lam}} = 275$ W/m$^2$K.
Figure 24: Comparison of complete model to experimental data for thermocouple #0 (T0) embedded in 20-layer glass/epoxy part, using $h_{\text{lam}} = 275 \text{ W/m}^2\text{K}$.

Figure 25: Comparison of complete model to experimental data for thermocouple #8 (T8) embedded in 20-layer glass/epoxy part, using $h_{\text{lam}} = 275 \text{ W/m}^2\text{K}$.
Figure 26: Comparison of complete model to experimental data for thermocouple #16 (T16) embedded in 20-layer glass/epoxy part, using $h_{am} = 275$ W/m$^2$K.

Figure 27: Close-up comparison of complete model to experimental data for thermocouple #8 (T8).
As was seen in the previous verification stage, the temperature predictions during
the initial layers of the experiment overestimate the values obtained during the
experiment (Figure 24). It was suspected that temperature fluctuations in the heated
laminator might be the cause. The fluctuations in laminator temperature were observed,
but not measured in this portion of the study. The temperature of the heating pad was
controlled using a standard PI controller. During the steps of the cycle that lamination
was not taking place, the laminator pad would remain relatively steady around the set
point of 130°C. During lamination of the first few layers of the material, a sharp decrease
in the temperature of the laminator was observed. The temperature would return to the set
point temperature approximately 30 seconds into the lamination. In the first three layers,
this temperature decrease was approximately 15-20°C. As the process proceeded, this
temperature drop became less pronounced and eventually disappeared by the eighth layer.
This observation explains the thermal phenomena that were seen in initial phases of the
heat transfer experiments for the glass/epoxy prepreg as well as the ceramic tape. The
heat transfer coefficient boundary condition attempts to represent the imperfect thermal
contact between the laminator and the part. However, this type of boundary condition
assumes that the temperature at a location beyond the point of contact remains constant.
This observation shows that this assumption is invalid; thus this type of boundary
condition cannot represent exactly the heat transfer dynamics of the laminator.

The model was also run without the source heat term included. The results of this
analysis graphically illustrated in Figure 28 show minimal, but observable, differences in
heat generation throughout the build. The temperature of the bottom layer at the end of
the build is approximately 5°C higher with the reaction than without. The same
temperature difference was seen for the other layers despite differences in the rate of cure and the degree of cure in each layer. This can be attributed to observation that the complete part temperature approaches a single value (i.e. a small (1-2°C) temperature gradient through the part) in the final layers. This result also suggests that the heat generation term in the equation of energy is minor relative to the heat conduction term, but it is not insignificant enough to exclude from the analysis for this particular material. Thus in making the quantitative assessment of the results of the model, it is important to include the heat source term into the Curved LOM simulation.

![Figure 28](image.png)

**Figure 28:** Comparison of model results with and without the cure sub-model for thermocouple #0 (T0) embedded in 20-layer glass/epoxy part.
5.4 Cure Sub-Model Results

Simultaneous cure rate and degree of cure calculations can be performed by the Curved LOM model. The model is able to predict cure distributions throughout the part using the cure sub-model programmed to estimate heat generation. The degree of cure results produced by the Curved LOM model are shown in Figure 29. The graph illustrates the spatial cure distribution at the end of every fourth layer cycle (i.e. every 360 seconds). These results are unverified from the experimental Curved LOM simulation, but they illustrate the utility that such a model possesses. The graph shows that the layers near the bottom of the part are more fully cured than the top layers at any given time. As the Curved LOM simulation progresses, a perceptible, constant, and significant cure gradient is also observed. Such predictions can be very helpful in terms of the manufacture of composite laminates. Experience with the Curved LOM process and manufacture of polymer composites has shown that the amount of cure that a given material undergoes can have a profound effect on the ultimate processability and final laminate properties, such as fiber volume fraction and mechanical properties. The ability of this model to predict cure distributions can allow one to tailor the conditions of the Curved LOM build or the starting material to obtain the ultimate result that is desired. Thus, the utility of including a cure model into the final Curved LOM model goes beyond the initial temperature predictions. The results of the cure model can also play an important role in the determination of the Curved LOM process conditions.

Verification of the cure distribution throughout the part thickness was beyond the scope of this study; however, there are two potential trials that can be performed to confirm these profiles. One possible experiment is to perform DSC scans on the top and
bottom layers of the laminate upon ending the cyclic lamination at the appropriate times to obtain the residual heat of reaction. While this would verify the high and low cure values, one would have to infer the appearance of the cure profile through the entire part. A method for verifying the cure distribution through the thickness of the part is to make simultaneous on-line dielectric measurements during the Curved LOM build. There are different ways to accomplish this such as by placing two electrodes slightly apart from each other on the same layer of the build or by using commercial interdigitated comb sensors. The dielectric loss factor can be measured and related to the cure state of the polymer [63]. To establish the relationship between the dielectric loss factor and the cure state of the epoxy resin, Dielectric Thermal Analysis (DEA or DETA) can be performed on the composite material.

![Graph showing cure sub-model results](image)

**Figure 29:** Cure sub-model results throughout part using $h_{\text{lam}} = 275 \text{ W/m}^2\text{K}$. 
A complete mathematical model for the thermal aspects of processing polymer matrix composite materials with the Curved LOM process was successfully developed. The model predicts spatial and temporal temperature and cure distribution of parts during fabrication. The model, based on one-dimensional transient heat conduction in thin panels, accurately predicts the qualitative features expected of a thermally cyclic process. The numerically computed results for a single layer were compared to an available analytical solution with good agreement. To verify the complete model, experimental data was collected from an off-line Curved LOM process. The heat transfer coefficient of the laminator to the part top surface was used as a model tuning parameter. Excellent quantitative agreement with most of the experimental observations was obtained. Thus, the approach to modeling the thermal nature of the Curved LOM process was deemed valid.

From a thermal perspective, the predictions made by the model provide some important observations about the nature of the process itself. To begin with, the heat transfer through the LOM paper mandrel was investigated to determine the effect of modeling the heat transfer boundary with a heat transfer coefficient. The results demonstrate that the assumptions made in the initial model may not necessarily apply when the conduction within the LOM-paper block is predicted. For example, since the
LOM-paper mandrel was significantly thicker than the final part being fabricated, the assumption of a thin part in this analysis may not result in accurate predictions. Also, perfect thermal contact between the part and the mandrel may not be achieved in the build. Also, the model predicted temperatures early in the experiment that were higher than what was measured in the Curved LOM experiments. This error was attributed to temperature fluctuations in the laminator as well as the support mandrel. These observations show the limitation of using the heat transfer coefficient boundary condition for a process that is essentially conductive.

As a part of the study, a kinetic analysis of a specific glass/epoxy prepreg was performed. The selected autocatalytic kinetic model matched the collected isothermal DSC data for a majority of the response. However, the model deviates furthest from the experimental data in the early stages of cure, where the kinetic predictions would be expected to be most important. This appears to be a function of several factors. First, the apparent shape of the experimental data suggests that the overall kinetic order of the reaction is higher that the assumed value of two. Also, the analysis suggests that the approach to determining the kinetic values, while being a relatively rapid means for estimating these values, is not the most accurate approach. A more rigorous approach to determining the kinetic parameters may provide more accurate results. Despite these inaccuracies, the Curved LOM model was still able to accurately predict the temperature distribution throughout the part thickness.

The results of the kinetic analysis were integrated into the Curved LOM model to determine cure distributions throughout the part. While these results were not directly verified, a basis for the accuracy of these predictions is provided by a DSC half-life
experiment performed on the glass/epoxy prepreg. While the temperatures produced by the model suggest that the heat generated within the part is not significant, the cure profiles do reveal the advantage of including the cure model in the Curved LOM model. The cure model provides a tangible and useful element to the Curved LOM model. The physical nature of the final laminate produced on the Curved LOM machine is ultimately determined by the thermal aspects of the process. The ability to predict the cure distribution throughout the part can aid in selecting the appropriate cycle parameters for the process. Thus, the overall Curved LOM model can serve a central role in a scheme for developing various advanced materials for the Curved LOM process and determining machine operating conditions. Currently, a trial and error approach is applied to the process to obtain the desired result. The ultimate objective is to have a completely automated process that requires a very low amount of human interaction. It is hoped such a model can be incorporated into an expert system that will provide the desired machine parameters from material characteristics. Even without such a system, the capability of this model to make temperature and cure predictions in this fashion will ultimately accelerate the adaptation of composite materials to this fabrication process.
Based on the results of this study, the following recommendations are proposed for future research.

1. The measurement of the thermal properties of the material is critical to the accuracy of the model predictions. Standard methods for measuring the density, heat capacity, and kinetic parameters of a given composite material are in place. However, a standard method for determining the thermal conductivity of the prepreg is not available at this time. An investigation and evaluation of potential techniques for measuring the thermal conductivity of a selected material should be undertaken. Without an apparatus for measuring the thermal conductivity, the model will be unable to make accurate temperature predictions for the process.

2. A complete investigation of the effect of varying model parameters on the predictions made by the model would provide meaningful insight into the effect of these parameters on the process itself. Such an investigation should encompass changes in material properties, process temperatures, including the laminator temperature, base plate temperature, and surrounding air temperature, and the heat transfer coefficient and the base of the part. Only with such an investigation can one fully understand the heat
transfer dynamics that are occurring in the build. Such an investigation can allow one to troubleshoot any deviations from the expected behavior of the model.

3. A means for verifying the in situ cure distribution of a polymer composite during the cure process would provide an important connection to the cure predictions made by the Curved LOM model. Such predictions could potentially be measured by dielectric measurements, which can be measure in a manner similar to the temperature measurements. The dielectric properties of thermoset polymers change as cure progress. Determining the magnitude of one of these properties through the use of Dielectric Thermal Analysis can allow one to determine the experimental cure distribution of a part fabricated on the Curved LOM process.

4. An investigation into the nature of the heat transfer between the laminator to the part as well as the part to the base should be undertaken. The experimental results clearly indicate the laminator heat transfer coefficient boundary condition is insufficiently accurate in predicting the temperature of the part in the early stages of the experiment. A different boundary condition form may provide a more accurate prediction of the early stages of the experiment. The part to base heat transfer coefficient is also sufficiently suspect so as to warrant a study into the appropriate manner to represent the heat transfer at this boundary. Since the chosen boundary condition is an approximation, it cannot be expected to fully represent the heat transfer dynamics; however, there may be other approximations that may produce more accurate results.
APPENDIX A

Effect of Time, Pressure, and Temperature on the Thickness Change of LOM-Paper Blocks

The curved layer LOM process requires a rigid mandrel for each desired curved layer part. Depending on the necessary processing conditions for the curved part (i.e., lamination time, temperature, and pressure), the mandrel can be made with either low-grade or high-grade materials. The use of LOM paper for these mandrels has several significant advantages over high performance composites, metals, or ceramics. The low cost of the material and the ease and speed of producing paper mandrels on the flat-layer LOM make it the initially preferred choice for mandrel fabrication for curved processing. However, there are notable concerns with the durability and capability of LOM paper to maintain dimensional stability at high temperatures and heavy loading. This paper outlines a designed experiment that investigates and attempts to quantify the effects of time, pressure, and temperature on the stability of LOM paper parts. This analysis is based on that of Box, Hunter and Hunter. [64]. From this data, a better understanding of how much these parameters impact the thickness change of a paper tool will be obtained.

To perform the study, eight 3-inch square paper blocks were fabricated on the LOM 1015 using LPH-008 LOM paper, which has a thickness of 0.008 inches. The initial average thickness of each of the paper blocks was 1.010 ± 0.010 inches. The average was based upon thickness measurements taken on each the four sides of a block. Measurements within each block varied by approximately 0.010 inches. This
measurement technique was repeated for each of the blocks at ambient temperature before and after the experimental runs were completed. The only measurements made in the study were the thickness dimensions.

The processing trials were performed on a Tetrahedron MTP Model 1401 flat heated press. The platens of the press were leveled before use. In addition, the blocks were placed between two 1/8-inch sheets of rubber to assure that pressure uniformity was maintained across the part surface. The parameters of the designed experiment are shown in Table A-1. The hold times for the experiment were 1 hour and 10 hours, the pressures were chosen to be 15 psig and 75 psig, and the temperatures of the experiment were selected as 60°C and 120°C.

Table A-1: Designed Experiment, Schedule, & Parameter Levels

<table>
<thead>
<tr>
<th>Trial</th>
<th>t (hr)</th>
<th>P (psig)</th>
<th>T (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>+</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>-</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>+</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>-</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>6</td>
<td>+</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>7</td>
<td>-</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>8</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
</tbody>
</table>

Parameters:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Levels</th>
</tr>
</thead>
<tbody>
<tr>
<td>t (hr)</td>
<td>1      10</td>
</tr>
<tr>
<td>P (psig)</td>
<td>15     75</td>
</tr>
<tr>
<td>T (°C)</td>
<td>60     120</td>
</tr>
</tbody>
</table>

A matter that was also of concern when selecting these parameters was the ability of the curved-layer LOM machine to consolidate commercially available prepregs. The pressures used in these experimental trials were selected on the basis of the currently available pressure (15 psi) and the maximum conceivable pressure (70 psi) for the curved LOM laminator. The temperature range is easily achieved with the existing laminator.
The time range is that for a short and long cure cycle for a typical thermoset resin. The experiments were run in standard order and not duplicated.

The shrinkage values for each experiment are listed in Table A-2. From this data, an analysis of the effects of hold time, temperature, and pressure was completed.

### Table A-2: Data from Designed Experiment

<table>
<thead>
<tr>
<th>Trial</th>
<th>t</th>
<th>P</th>
<th>T</th>
<th>Thickness Before</th>
<th>Thickness After</th>
<th>% Shrinkage</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.0016</td>
<td>1.0016</td>
<td>0.00%</td>
</tr>
<tr>
<td>2</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>1.005</td>
<td>0.9935</td>
<td>1.14%</td>
</tr>
<tr>
<td>3</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>1.015</td>
<td>0.9975</td>
<td>1.72%</td>
</tr>
<tr>
<td>4</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>1.02</td>
<td>0.9785</td>
<td>4.07%</td>
</tr>
<tr>
<td>5</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>1.02</td>
<td>0.9225</td>
<td>9.56%</td>
</tr>
<tr>
<td>6</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>1.015</td>
<td>0.9055</td>
<td>10.79%</td>
</tr>
<tr>
<td>7</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>1.015</td>
<td>0.885</td>
<td>12.81%</td>
</tr>
<tr>
<td>8</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>1.015</td>
<td>0.865</td>
<td>14.78%</td>
</tr>
</tbody>
</table>

The main effects of each of these variables are tabulated in Table A-3 and graphically shown in Figures A-1, A-2, and A-3. First, the data shows that an increase in any one of these variables leads to increased shrinkage in the thickness as expected. It is also apparent that temperature has a more significant effect on shrinkage than pressure or hold time. Including experimental measurement error, the temperature is still the most prominent main effect in the experiment. Interaction effects are shown in Table A-4. The data in Tables A-3 and A-4 is given in percent shrinkage. Figures A-4, A-5, and A-6 illustrate these effects graphically. The parallel nature of the lines indicates that there are minimal or no interactions between any two variables in the experiments.

### Table A-3: Main Effect Parameters

<table>
<thead>
<tr>
<th>Main Effects</th>
<th>-</th>
<th>+</th>
<th>y, (av)</th>
<th>y, (av)</th>
<th>Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>t (hr)</td>
<td>1</td>
<td>10</td>
<td>6.02%</td>
<td>7.69%</td>
<td>1.67%</td>
</tr>
<tr>
<td>P (psig)</td>
<td>15</td>
<td>75</td>
<td>5.37%</td>
<td>8.34%</td>
<td>2.97%</td>
</tr>
<tr>
<td>T (°C)</td>
<td>60</td>
<td>120</td>
<td>1.73%</td>
<td>11.98%</td>
<td>10.25%</td>
</tr>
</tbody>
</table>
Table A-4: Two Level Interaction Parameters

<table>
<thead>
<tr>
<th>Two Level Interactions</th>
<th>Time -</th>
<th>Time +</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure -</td>
<td>4.78%</td>
<td>5.97%</td>
</tr>
<tr>
<td>Pressure +</td>
<td>7.27%</td>
<td>9.42%</td>
</tr>
<tr>
<td>txP Interaction</td>
<td>2.49%</td>
<td>3.46%</td>
</tr>
<tr>
<td>Time -</td>
<td>0.97%</td>
<td></td>
</tr>
<tr>
<td>Time +</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature -</td>
<td>0.86%</td>
<td>2.61%</td>
</tr>
<tr>
<td>Temperature +</td>
<td>11.18%</td>
<td>12.78%</td>
</tr>
<tr>
<td>txT Interaction</td>
<td>-0.14%</td>
<td></td>
</tr>
<tr>
<td>Pressure -</td>
<td>0.57%</td>
<td>2.90%</td>
</tr>
<tr>
<td>Pressure +</td>
<td>10.17%</td>
<td>13.79%</td>
</tr>
<tr>
<td>PxT Interaction</td>
<td>9.60%</td>
<td>10.90%</td>
</tr>
<tr>
<td></td>
<td>1.30%</td>
<td></td>
</tr>
</tbody>
</table>

Based on these preliminary results, it appears that the temperature of hold application has the most significant affect on the dimensional stability of LOM paper tooling. This data also shows that the amount of pressure applied also plays a minor role in the thickness change of the paper blocks. One other significant piece of information that can be drawn from this data is that hold time and the interactions between these three factors have a minor impact or no impact on the shrinkage of the block thickness. The maximum acceptable shrinkage of the mandrel has to be determined from part to part, depending on the user’s applications and requirements.

With regard to using this material as a mandrel for curing the low temperature curing epoxy prepreg (LTM 45-EL [65]), this data suggests that paper is a suitable material if 2% shrinkage is tolerable. However, for other materials in the LOM process, there are still some concerns and some missing parameters to investigate. Since LOM is a repetitious process, cyclic loading along with the interactions of cyclic loading with
pressure, temperature and time must also be investigated. Also, it is not clear as to whether the change of thickness is linearly dependent to these parameters. Notice that the y intercept of the lines for Figures A-1 and A-2 are not zero. This may suggest that an initial seasoning of an LOM-paper mandrel can reduce total shrinkage during the Curved LOM processing. Further experiments must be performed to refine the correlation of shrinkage of LOM paper with temperature. This data will allow a processing window to be determined in which paper can be reliably used as tooling.

Figure A-1: Main Effect of Time on Shrinkage
Figure A-2: Main Effect of Pressure on Shrinkage

Figure A-3: Main Effect of Temperature on Shrinkage
Figure A-4: Interaction Effect of Time and Pressure on Shrinkage

Figure A-5: Interaction Effect of Time and Temperature on Shrinkage
Figure A-6: Interaction Effect of Pressure and Temperature on Shrinkage
APPENDIX B
Curved LOM Model Program Listing in FORTRAN

PROGRAM LOMTHERM

One-Dimensional Thermal Model for Curved-layer Laminated Object Manufacture of PMC's.

Eric Bryant

COMMON /CONST/CK,RHO,CP,ALPHA,HP
COMMON /STEPS/L,DZ,DTAU,TAU
COMMON /VAR/T(41),HR(41),CVZ(41)
COMMON /TEMPS/TZ1,TZ2
COMMON /HEAT/HDZ1,HDZ2
COMMON /RATIOS/RATIOZ
COMMON /ROLLER/JLO,RTZ1,RHDZ1

Material properties

CK=0.31E-3
RHO=1.70E3
CP=1.39
ALPHA=CK/(RHO*CP)
HP=106.5
DEGC0=0.0

Initial number of nodes in the z-direction
L=3

Grid size
DZ=0.00011

Heat transfer coefficients for 2 surfaces
HZ1=13.6E-3
HZ2=8.5E-3
HDZ1=2.0*HZ1*DZ/CK
HDZ2=2.0*HZ2*DZ/CK

Bulk Temperatures of surroundings for 2 faces.
TZ1=15.0
TZ2=15.0
Initialize variable arrays for entire solution region.

T0=15.0
DO 2 K=1,L
   CVZ(K)=DEGC0
2   T(K)=T0

Initialize laminator variables

JLO=0
HOLD=40.0
RTZ1=130.0
RHZ1=275.0E-3
RHDZ1=2.0*RHZ1*DZ/CK

Open files for results (plot data).

OPEN (10,FILE='pmctem01.DAT',STATUS='UNKNOWN')
OPEN (20,FILE='pmccur01.DAT',STATUS='UNKNOWN')
OPEN (30,FILE='curpro01.csv',STATUS='UNKNOWN')

Initialize time

TAU=0.0

Delay before laminating new layer.

10 DTAU=1.0
   DELAY=10.0
   RATIOZ=DTAU/(DZ*DZ)
   LOOP6=INT(DELAY/DTAU+0.5)
   DO 25 II=1,LOOP6
      CALL TEMP
      TAU=TAU+DTAU
      CALL OUTPUT
25 CONTINUE

Start laminator hold

DTAU=0.1
   RATIOZ=DTAU/(DZ*DZ)

Calculate iterations required for laminator hold.

LOOP1=INT(HOLD/DTAU+0.5)
   DO 1 II=1,LOOP1

Change value of the Heat Transfer Coefficients for the top layer.

TZ1=RTZ1
HDZ1=RHDZ1
Call subroutine to determine heat release and advance
temperature distribution by one time increment DTAU.

CALL TEMP

Advance time by one increment DTAU

TAU=TAU+DTAU
CALL OUTPUT

1 CONTINUE

Delay before adding new layer (laser cut)

TZ1=15.0
HDZ1=2.0*HZ1*DZ/CK
DTAU=0.1
DELAY=40.0

RATIOZ=DTAU/(DZ*DZ)

LOOP4=INT(DELAY/DTAU+0.5)

DO 14 II=1,LOOP4
CALL TEMP
TAU=TAU+DTAU
CALL OUTPUT
14 CONTINUE

Add new layer if less than 20 layers

IF (L.LT.40) THEN
L=L+2
DO 6 K=L,3,-1
CVZ(K)=CVZ(K-2)
6 T(K)=T(K-2)
CVZ(1)=DEGCO
CVZ(2)=DEGCO
T(1)=T0
T(2)=T0
5 T(3)=(T(3)+T0)/2.0
ELSE

Close data files and terminate execution.

CLOSE(10)
CLOSE(20)

Print out final cure profile
CALL PROFILE
CLOSE(30)
STOP
ENDIF

Return to start for new layer
SUBROUTINE OUTPUT

Subroutine to output results to appropriate data files.

COMMON /VAR/T(41),HR(41),CVZ(41)
COMMON /STEPS/L,DZ,DTAU,TAU

WRITE(*,99) TAU,L,T(L-1)
99 FORMAT(' TIME = ',F10.2,' NODES = ',I2,' T = ',F10.3)

IF ((TAU.GE.359.90).AND.(TAU.LT.360.00)) THEN
   CALL PROFILE
ELSEIF ((TAU.GE.719.90).AND.(TAU.LT.720.00)) THEN
   CALL PROFILE
ELSEIF ((TAU.GT.1079.90).AND.(TAU.LE.1080.00)) THEN
   CALL PROFILE
ELSEIF ((TAU.GT.1449.70).AND.(TAU.LE.1449.80)) THEN
   CALL PROFILE
ELSE
   END IF

IF (L.LT.10) THEN
   WRITE(10,100) TAU,T(L-1)
   WRITE(20,100) TAU,CVZ(L-1)
100 FORMAT(F10.2,F10.3)
ELSEIF (L.LT.18) THEN
   WRITE(10,101) TAU,T(L-1),T(L-9)
   WRITE(20,101) TAU,CVZ(L-1),CVZ(L-9)
101 FORMAT(F10.2,2F10.3)
ELSEIF (L.LT.26) THEN
   WRITE(10,102) TAU,T(L-1),T(L-9),T(L-17)
   WRITE(20,102) TAU,CVZ(L-1),CVZ(L-9),CVZ(L-17)
102 FORMAT(F10.2,3F10.3)
ELSEIF (L.LT.34) THEN
   WRITE(10,103) TAU,T(L-1),T(L-9),T(L-17),T(L-25)
   WRITE(20,103) TAU,CVZ(L-1),CVZ(L-9),CVZ(L-17),CVZ(L-25)
103 FORMAT(F10.2,4F10.3)
ELSE
   WRITE(10,104) TAU,T(L-1),T(L-9),T(L-17),T(L-25),T(L-33)
   WRITE(20,104) TAU,CVZ(L-1),CVZ(L-9),CVZ(L-17),CVZ(L-25),CVZ(L-33)
104 FORMAT(F10.2,5F10.3)
ENDIF

RETURN

END
**SUBROUTINE TEMP**

Subroutine to calculate the heat release of the material and to advance temperature distributions by one time increment DTAU.

>> Rectangular geometry. <<

Compute temperatures at the nodes

```
COMMON /CONST/CK,RHO,CP,ALPHA,HP
COMMON /STEPS/L,DZ,DTAU,TAU
COMMON /VAR/T(41),HR(41),CVZ(41)
COMMON /TEMP/TZ1,TZ2
COMMON /HEAT/HDZ1,HDZ2
COMMON /RATIOS/RATIOZ
COMMON /ROLLER/JLO,RTZ1,RHDZ1

DIMENSION A(50),B(50),C(50),E(50),TP(50),RK1(41),RK2(41)
DIMENSION RATEN(41),RATENN(41),CVZP(41)
```

Calculate Heat of Reaction Produced in Time Increment

give Activation energies as EA1=Ea1/R, EA2=Ea2/R

EA1=-8.1227E+03
EA2=-8.4506E+03
AF1=14.873E+06
AF2=0.37425E+09
EM=0.6913
EN=1.3087

DO 30, I=1,L

```
RK1(I)=AF1*EXP(EA1/(T(I)+273.15))
RK2(I)=AF2*EXP(EA2/(T(I)+273.15))
RATEN(I)=(RK1(I)+(RK2(I)*(CVZ(I)**EM)))*(1.0-CVZ(I))**EN
CVZP(I)=CVZ(I)+RATEN(I)+DTAU
RATENN(I)=(RK1(I)+(RK2(I)*(CVZP(I)**EM)))*(1.0-CVZP(I))**EN
HR(I)=HP*(RATENN(I)+RATEN(I))/120.0
CVZ(I)=CVZ(I)+DTAU*(RATEN(I)+RATENN(I))/120.0
```

Set up coefficients for tridiagonal matrix

```
AA=-ALPHA*RATIOZ
BB=2.0*ALPHA*RATIOZ+1.0
```

DO 6 K=1,L

```
IF (K.EQ.1) THEN
  B(K)=BB-HDZ1*AA
  C(K)=2.0*AA
  E(K)=-HDZ1*AA*TZ1
ELSEIF (K.EQ.L) THEN
  A(K)=2.0*AA
```

```
B(K) = BB - HDZ2 * AA
E(K) = - HDZ2 * AA * T2
ELSE
A(K) = AA
B(K) = BB
C(K) = AA
E(K) = 0.0
ENDIF

6 E(K) = E(K) + T(K) + H(K) * DTAU / CP

Solve Tridiagonal matrix to obtain temperature distribution

CALL TRIDAG (1, L, A, B, C, E, TP)
DO 5, K = 1, L
5 T(K) = TP(K)

RETURN
END

***************************************************************************************
SUBROUTINE TRIDAG (IF, L, A, B, C, E, V)
Used by S/R TEMD. Solves a system of simultaneous linear equations having tridiagonal coefficient matrix.
Taken from Carnahan, Luther and Wilkes, Pg. 446. (Thomas Method)
DIMENSION A(1), B(1), C(1), E(1), V(1), BETA(50), GAMMA(50)

BETA(IF) = B(IF)
GAMMA(IF) = E(IF) / BETA(IF)
IFF1 = IF + 1
DO 1 I = IFF1, L
BETA(I) = B(I) - A(I) * C(I - 1) / BETA(I - 1)
1 GAMMA(I) = (E(I) - A(I) * GAMMA(I - 1)) / BETA(I)
V(L) = GAMMA(L)
LAST = L - IF
DO 2 K = 1, LAST
I = L - K
2 V(I) = GAMMA(I) - C(I) * V(I + 1) / BETA(I)

RETURN
END

***************************************************************************************
SUBROUTINE PROFILE
Used by S/R OUTPUT. Produces output of cure profile at the given time called
COMMON /VAR/T(41), HR(41), CVZ(41)
COMMON /STEPS/L, DZ, DTAU, TAU
DO 95 I = 1, L
WRITE (30, 110) TAU(I), CVZ(I)
110 FORMAT (1X, F10.2, ',', F10.3)
95 CONTINUE
C
RETURN
END
C
C*****************************************************************************
APPENDIX C

Development of Equations used to Estimate Cure Model Parameters [56]

In most cases, linear and non-linear least squares fitting techniques are used to estimate the parameters of the kinetic rate relation. This requires a detailed and precise data on the reaction rate as a function of time for a given constant temperature. However, the equations described here simply require reaction rate data at the beginning of the experiment and at peak reaction rate for a given temperature. Use of these characteristic points of the reaction rate curve can provide a simple, but accurate, estimation of the kinetic parameters. The convergence of certain non-linear regression techniques often depends on an initial estimate, which can be determined by this method.

An equation used to describe the kinetics of autocatalytic curing reactions is:

\[ \frac{d\alpha}{dt} = (k_1 + k_2\alpha^n)(1-\alpha)^n \]  

This equation can be rearranged in terms of the exponent \( m \) as follows:

\[ m = \frac{\ln \left( \frac{\frac{\alpha}{(1-\alpha)^n} - k_1}{k_2} \right)}{\ln \alpha} \]  

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Applying an initial condition of $t=0$ and $\alpha=0$, the reaction rate is defined by rate constant $k_1$. Thus, the equation reduces to:

$$\left( \frac{d\alpha}{dt} \right)_{t=0} = k_1$$

(3)

This result implies that the reaction rate constant $k_1$ can be directly determined from the isothermal reaction rate data.

The peak reaction rate is defined by the condition:

$$\frac{d}{dt} \left( \frac{d\alpha}{dt} \right) = 0$$

Applying this condition to the kinetic rate expression produces the following expression:

$$nk_1 \alpha_P^{1-m} + k_2 (m+n) \alpha_P - mk_2 = 0$$

(4)

In this equations and subsequent equations, the subscript P refers to the value at the time of the peak reaction rate. In most cases, the kinetics of epoxy cure have been successfully described by an overall second-order kinetic expression. Therefore, the sum of the exponents, $m$ and $n$, are set to equal two. Using this assumption, the previous equation can be rearranged for $k_2$ as follows:

$$k_2 = \frac{(2-m)k_1 \alpha_P^{1-m}}{m-2\alpha_P}$$

(5)

Replacing the expression for $k_2$ into equation (2), one obtains:

$$m = \frac{\ln \left( \frac{\alpha_P}{(1-\alpha_P)^{1-m}} - k_1 \right)}{\ln \alpha_P}$$

(6)
The only value in equation (6) that is not directly produced from an isothermal experiment is the exponent m. From experimental data, one can calculate the value of m using numerical root finding techniques and use this value to calculate $k_2$ using equation (5).
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53. The Jerico Company
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