Chemical Kinetics and Heat Transfer in Polyurethane Foam and Resin Composites

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CHEMICAL KINETICS AND HEAT TRANSFER IN POLYURETHANE FOAM AND RESIN COMPOSITES

by

Yumi Morisaki

A Thesis Submitted to the Graduate Studies Office in Partial Fulfillment of the Requirements for the Degree of Master of Science in Aerospace Engineering

Embry-Riddle Aeronautical University
Daytona Beach, Florida
Summer, 1998
UMI Number: EP31829

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This thesis was prepared under the direction of the candidate's thesis committee chair, Dr. Yechiel Crispin, Department of Aerospace Engineering, and has been approved by the members of his thesis committee. It was submitted to the Department of Aerospace Engineering and was accepted in partial fulfillment of the requirements for the degree of Master of Science in Aerospace Engineering.
ACKNOWLEDGMENTS

I would like to express my gratitude to the individuals who have helped me accomplish my thesis.

My greatest appreciation and respect go to Dr. Yechiel Crispin, Chair of my thesis committee, for his guidance, his encouragement, his patience, his humor, and his knowledge in this topic and in the use of MATLAB software. I would also like to appreciate Dr. Crispin and Florida Space Grant Consortium for providing me with the financial support for my graduate studies.

I would like to give special thanks to Boston Whaler for providing me with the valuable experimental data.

I would like to express my appreciation for the guidance and contributions made by my thesis committee members, Dr. L. Reisbig and Dr. L. Narayanaswami.

This statement of acknowledgment would be incomplete without expressing my sincere appreciation and gratitude to both my friends and family. I would like to thank How Meng, Andrew, Veronique, Marianne, Chen, Jintark, Hideyo, and Estelle for their encouragement during my research work, and their concerns about my health problem. I would like to express my appreciation for Mrs. Alice Chiellini, who has offered so many helps in and outside the school for the past five years. I would particularly thank my family, Toshiyuki, Mitsuko, Maki, S.M, and O.M, for their continuous support, encouragement, and understanding throughout my entire school career.
ABSTRACT

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Year: 1998

A development of the composite materials parts require knowledge of the theoretical model that describes the physics, the chemical kinetics, and the heat-transfer properties of the materials.

For this work, the chemical kinetics of the polyurethane foam and the fiberglass-reinforced resin is investigated individually. An adiabatic method, which is commonly used by many investigators, is used for the polyurethane foam, while an isothermal degree and the rate of cure relationship is applied for the resin. A heat transfer effect during the curing process of both polyurethane foam and the resin is also investigated. A common approximate method for the heat-conduction problem known as a 'heat-balance integral method,' is considered with several assumptions to simplify the analysis.

The experiments involving a wooden box mold, which produces a sandwich construction of a polyurethane foam by the fiberglass-reinforced resins was performed at Boston Whaler facility by another individual. The temperature profiles of the polyurethane foam, the resin, and the mold were obtained for the purpose of analyzing the chemical kinetics and the heat transfer properties of the foam and the resin.
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NOMENCLATURE

Chapter 3: Analysis of the Polyurethane Foam Chemical Reaction

A frequency factor (characteristic reaction time)
B₀ autocatalysis intensity
C₀ initial concentration of isocyanate
Cₚ heat capacity per unit volume
E Eₐ/R
Eₐ activation energy
n reaction order
R gas constant
t time
T temperature at a given time
Tᵣ final temperature (maximum temperature)
Tₘₐₓ maximum temperature (=final temperature)
Tₘ₀ temperature at where maximum dT/dt occurs
T₀ initial temperature
x fractional monomer conversion
(ΔH)ᵣ heat of reaction

Chapter 3: Analysis of the Polyurethane Foam Heat Loss

A heat transfer area
Cₚᵤ heat capacity at constant pressure
h heat transfer coefficient
h* h₄/M
M mass of the reacting mixture
Tₐ ambient temperature

Chapter 4: Analysis of the Fiberglass-Reinforced Resin Chemical Reaction

A₁, A₂ pre-exponential factors
c specific heat capacity
(dQ/dt)ᵢ instantaneous rate of heat generation at isothermal condition
dβ/dt isothermal rate of cure
H₁ isothermal heat of reaction
K₁, K₂ reaction rate constants
m mass of the resin
m & n orders of reaction
Q amount of heat generated in a given time t
R gas constant
t time
\( t_{fr} \)  
- time at which no more heat generation can be observed at the constant temperature of the experiment

\( T \)  
- cure temperature (in Arrhenius relationship) or temperature of the resin at a given time

\( T_f \)  
- final temperature

\( T_0 \)  
- initial temperature

\( \beta \)  
- isothermal degree of cure

\( \Delta E_1, \Delta E_2 \)  
- activation energies

\( \Delta T \)  
- temperature difference at a time of interest

\( \rho_r \)  
- density of the resin

**Chapter 5: Preliminary Analysis of the Interactions between the Polyurethane Foam and the Resin**

\( A, B, C \)  
- constants in temperature distribution equation of the resin

\( C_p \)  
- specific heat capacity (denoted as \( C_f \) and \( C_r \) for two materials)

\( f(x) \)  
- cure kinetics model of polyurethane foam

\( f(\beta) \)  
- cure kinetics model of resin

\( g(t) \)  
- heat generation by resin chemical reaction

\( h \)  
- thickness of the resin

\( H_r \)  
- specific ultimate heat of reaction of the resin

\( H_f \)  
- specific ultimate heat of reaction of the foam

\( K \)  
- thermal conductivity (subscripts \( f \) and \( r \) represents that for the foam and the resin)

\( t \)  
- time

\( T \)  
- temperature of the resin during the interaction (also shown with subscript \( r \))

\( T_a \)  
- ambient temperature

\( T_f(t) \)  
- foam temperature as a function of time

\( y \)  
- location inside the resin

\( \alpha \)  
- thermal diffusivity

\( \delta(t) \)  
- thermal layer thickness

\( \rho_f \)  
- density of the foam

\( \rho_r \)  
- density of the resin
CHAPTER 1

Introduction

1.1 Background

Composite materials have become an essential part of the modern society, with applications ranging from aerospace, automotive, marine, architectural structures, to household consumer products. Although the history of composite materials dates back as far as 12th century, what have changed dramatically in modern days are that a greater number of materials are available and new processes have been developed to combine these materials to make composites with improved properties. The use of the composite materials have many advantages over other materials such as metals and glasses. These advantages include corrosion resistance, electrical and thermal insulation, lower weight and smoother surface of the finished products. These are particularly important in aerospace, automotive, and marine applications in designing the high-performance and the fuel-efficient vehicles.

A composite material may be defined as a combination of two or more materials (reinforcing elements, fillers, and composite matrix binder), differing in form or composition on a macroscale. For instance, polyurethane foam, a reaction product of an isocyanate, a polyol, and a curing agent, may be applied over the fiberglass-reinforced resin to create a durable and light-weight composite materials plate, which is used by boat manufacturers. The resin, an essential material associated with composites, is defined as a solid or pseudo-solid organic material, usually of high molecular weight, that exhibits a tendency to flow when subjected to a stress. Most resins are polymers, and they usually have softening or melting ranges. In reinforced plastics, the resin is the material used to bind together the reinforcement material. Polyurethane foam, as described before, is one of the thermosetting resins.
The development of composite materials parts requires knowledge of physics, chemical kinetics, and heat transfer properties of the material that is being studied. For instance, studies of the foam curing process, such as cycle times and mold cooling requirement, process modeling, including predictions of pressure requirements during filling, conversion/temperature profiles, and demold times during curing, all require a kinetic information of the polymer be known. The product development, such as the catalyst evaluation, systems comparison, and variations in composition may also be studied using the chemical kinetics. At the same time, the heat transfer plays an important role in the curing process, such as in the polymer reaction molding operations like casting, thermoset molding or reaction injection molding (RIM), with mold temperature controlled by the fluid circulation over the mold wall. The heat transfer through the wall accelerates the rate of reaction of the polymer inside, resulting in efficient production of the composite material.

Extensive investigations have been carried out over the past several decades on the chemical kinetics of the polyurethane foam and the resin, as well as the heat transfer effects on these materials through the heated mold. These investigations provide the foundation for the work done for this thesis, and the details will be discussed in the next section.

1.2 Introduction to the Present Work

In order to study the chemical kinetics and the heat transfer properties of the polyurethane foam and the resin, three experiments were performed using the wooden box mold, which produced a sandwich construction of a polyurethane foam by the fiberglass-reinforced resin. The foam was applied over the resin while the resin was in various curing stages; gelled, wet, and fully cured. The temperature profiles of the polyurethane foam, the resin, and the mold were obtained for the purpose of analyzing the chemical kinetics and the heat transfer properties of the foam and the resin. The details of the experimental set up and the data analysis will be discussed in Chapter 2.
An adiabatic method has been widely used by several investigators as an indirect method to measure the reaction kinetics of the polyurethane foam. Fast reacting exothermic systems, such as those used in the reaction injection molding, are usually treated to be adiabatic, or nearly adiabatic systems, and their reaction kinetics can be studied with the indirect method. Camargo [Camargo, 1982, 1984] and Macosko [Macosko, 1989] have done many experiment on adiabatic systems, using polypropylene cup and several thermocouples to measure the temperature of the polymer reactant. In many cases, the temperature history of the reactant obtained from the experiment had very good agreement with that obtained by an adiabatic method (i.e., reaction kinetics in the energy equation defining the temperature history of the polymer). In Chapter 3, the temperature of the polymer containing isocyanate and polyol is considered. An adiabatic method is directly applied to analyze the reaction kinetics of the polyurethane foam. A nonlinear least-squares curve fit is applied to the experimental temperature profile of the foam to obtain the kinetic constants in the theoretical model. The models known as the n-th order and the auto-catalytic are both tested for their fittings to the experimental data. A heat loss, which takes place after the foam attains the maximum exothermic temperature, is also analyzed.

In recent years, analytical modeling has been proven to be successful in selecting appropriate temperatures and pressures for the curing of organic matrix composites. An equipment called a differential scanning calorimeter has been widely used to generate the data for the degree of cure, the rate of cure, and the heat of reaction of the resin that is being studied. Two different experiments, in which data are taken at an isothermal condition (isothermal scanning) and at a constant heating rate (dynamic scanning), are necessary in order to study the cure kinetics of the resin. In Chapter 4, the chemical kinetics model for the resin reaction is considered. The nonlinear least-squares curve fit to the experimental temperature profile of the resin is used to analyze the kinetic constants in the theoretical model. The relationships between the isothermal degree and the rate of cure is used to define the theoretical temperature profile.

Heat transfer has been a focus of the polymer curing process, along with the chemical kinetics. Heat applied through the mold accelerates the reaction of a polymer
inside, resulting in more efficient production of the composite material. Many researchers have studied the heat transfer effects through the mold on the polymer. In Chapter 5, heat transfer from the reacting polyurethane foam into a curing resin is considered. However, because of the complexity in the formulation of the problem, the result is not presented in this thesis. Rather, several possibilities in analyzing the problem is considered, based on the law of conservation of energy together with an appropriate expression for the cure kinetics of the polyurethane foam and the resin. A coupled energy equations for the foam and the resin are introduced, along with the appropriate number of the boundary conditions. Another possibility using the approximation method for the heat conduction problem known as a 'heat balance integral method' is considered. A simplified boundary condition is applied to the boundary-value problem of heat conduction involving a heat generation. The procedure for this method is discussed up to the point where several unknown constants are needed in order to proceed with the calculation.

This thesis ends with Chapter 6, which contains a conclusion of this work, and the recommendations for the future research work.
CHAPTER 2
Experiment Procedure and Data

In this chapter, experimental setup, procedure, and data used in this research work will be discussed. Figure of the box mold containing all of its measurements, and several plots of temperature profiles of polyurethane foam, resin, and box mold are introduced. These data will extensively be used in the analysis of the chemical kinetics in the following chapters. Most of these data were slightly modified for the purpose of distinguishing the reacting segment from the non-reacting one, and eliminating the fluctuations caused by the measuring instrument. The details of these modifications will be discussed in the following chapters.

2.1 Experimental Set Up and Procedure
In order to study and develop an optimized and innovative manufacturing process of composite materials parts, three experiments were performed using the wooden box mold. These experiments were performed at Boston Whaler facility by an undergraduate student. Figure 1 shows the geometry of the box mold. Exterior measurements of the mold are 63.88 inches (162.26cm) in length, 17 inches (43.18cm) in width, and 4.88 inches (12.4cm) in height. However, three inner sidewalls are slanted toward center for 0.63 inches (1.6cm). Height of the content (foam) is therefore about 2.12 inches (5.38cm), while maximum length and width are 60.25 inches (153.04cm) and 14 inches (35.56cm). Polyurethane foam of a type 'MDI XR-1842,' and a general purpose resin, reinforced with a mat of fiberglass, were to be analyzed during their chemical reactions in this box mold. First, a fiberglass mat is placed on the bottom of two box molds, and resin is applied over these mats. Then the foam is applied over those resins during their
Figure 1 Foam Box Mold

17.00"

63.88"

2.13"

0.63"

3.5"

1.38"

1.50"

2.13"

1.50"

2.13"
various curing stages. Two box molds are then put together to form a sandwich-type construction of a polyurethane foam and the fiberglass-reinforced resins.

For the first experiment, the procedure was similar to that of the production standards where the foam was added into the box mold when the resin was in a gelled curing stage. This stage may be referred to as the point in a resin cure when the resin viscosity has increased to a point such that it barely moves when probed with a sharp instrument. In general, gels are soft and flexible, having very low strengths, and do not flow like a liquid [Davis, 1992]. Total weight of 1400 grams of foam, that was slightly below the room temperature of 72.6 degrees Fahrenheit, was applied to 1816.95 grams of resin in gelled condition. This application of foam was performed one hour and eight minutes after the resin was catalyzed. The thermocouples were placed in top and bottom mold, resin, and foam, and temperatures were recorded every five seconds for nearly two hours by the data acquisition system.

For the second experiment, two separate cases were studied. One was to measure the temperatures of top and bottom fiberglass-reinforced resins, and top mold, during the chemical reaction of a resin. This experimental data was useful in determining the chemical kinetics constants in the defining equation, which relates the isothermal degree of cure, and rate of change of cure to the temperature of this specific resin at a given time. However, the data acquisition was continued for nearly four hours, until the peak of an exotherm temperature was obtained. The second case consisted of applying the foam to a resin that has cured completely, and to record the temperatures of top mold, top and bottom resins, and foam during the sole reaction of the foam.

The third experiment was somewhat similar to the first experiment, however the foam was applied when the resin was in wet curing stage. This stage may be referred to as the point in a cure, when the resin is saturated with absorbed moisture, or at a defined percentage of absorbed moisture less than saturation. A saturation is an equilibrium condition in which the net rate of absorption under prescribed conditions falls essentially to zero [Davis, 1992]. Temperatures of top and bottom resin, top mold, and foam were recorded for nearly two hours.
2.2 Data Analysis

Figure 2 shows the temperature profiles of top mold, top and bottom resins, and foam during the gelled curing stage of a resin. As it can be seen, the foam has started reacting fast, with the temperature increase of approximately 60 degrees Kelvin. The maximum temperature, or the peak of the curve of approximately 356 degrees Kelvin indicates the completion of a reaction of the foam. This temperature was achieved in 700 seconds. After reaching this peak, the foam starts to transfer its heat to the surroundings, however, it was observed that the foam was receiving some heat from the reacting resin around 1800 seconds. A temperature increase of approximately 5 degrees Kelvin was observed near the peaks of top and bottom resin temperature curves.

The top and the bottom fiberglass-reinforced resins seemed to have received heat from the reaction and the transfer from the foam, and thus started reacting much faster than when the curing was monitored with resin reacting just by itself. This difference may be observed in Figure 3, where the reaction of the resin is very time-consuming compared to that of Figure 2. An unsteady temperature increase of those resins seems to hold strong relationship with the changing surrounding temperature, which is a foam in

![Figure 2. Temperature Profile (Resin Gelled, Foam Applied)](image-url)
this case. This result can be compared to the temperature profile of a sole resin reaction of Figure 3, which has nearly steady temperature increase, once the reaction has initiated. Heat transfer processes are very smooth for both resins, after they have attained their maximum temperatures.

In the numerical analysis, which will be described in details in the following chapters, temperature profiles of the top and the bottom fiberglass-reinforced resins were treated to be the same. The wooden box mold has received very small influence from the reaction heat of these composite materials.

Figure 3 shows the temperature profiles of the top and the bottom resins, and the top mold. Low surrounding temperature, or the room temperature is abruptly delaying the initiation of a reaction, which in fact does not start for the first 6000 seconds, or one hour and forty minutes. Once the reaction has started taking place, a temperature increase for both top and bottom resins are very constant, until it reaches the peak of
approximately 300 degrees Kelvin. However, this reaction has taken nearly one hour and thirty minutes, indicating a reaction without an external heat source is very time consuming. This result can be compared to that of Figure 2 in which resin achieves a maximum temperature in approximately 2000 seconds, which is only 1/3 of the reaction by the resin itself. Although it was not a significant increase, it was observed that the mold temperature was directly influenced by the heat release of the resin.

The fluctuations of the data seemed to have resulted from the instability of the reaction due to the low surrounding temperature, and the measuring device. These fluctuations were eliminated before the data were analyzed, and various methods of noise elimination will be discussed in the following chapters.

Figure 4 shows the temperature profiles of foam, top and bottom resins, and top mold, when the foam was being applied to the resin that has cured completely. These data were mainly used for the purpose of analyzing the chemical kinetics of the polyurethane foam. The heat generation of the foam was as high as 85 degrees Kelvin, and has influenced the temperatures of top and bottom resins by raising their temperatures for approximately 15 degrees Kelvin. However, the mold had very small
influence from the heat generation of the foam. Because of the low surrounding
temperature, the foam did not start reacting for the first 80 seconds. The data during this
time interval were considered to be an insignificant heat loss, and were disregarded in the
analysis of the chemical kinetics. Approximately 420 seconds were needed in order to
achieve the maximum temperature of 380 degrees Kelvin, or to complete the reaction.
The data during this time interval were used in finding the kinetics constants in the
energy equation, which describe the characteristics of the foam used in this experiment.

A rapid heat loss, after reaching the maximum temperature, was also studied using
the energy equation, but without the contribution from the reaction.

Figure 5 shows the temperature profiles of foam, top and bottom resins, and top
mold, while the resin is in the wet curing stage. The temperature behaviors of foam and
resin are somewhat similar to that of Figure 2, however, a minor heat loss was observed
in the former case, before the resin has achieved its peak exothermic temperature. Top
and bottom resins have reached the maximum temperature of approximately 330 degrees
Kelvin, which is very similar to that of the Figure 2, when the resin was in gelled curing
stage. Foam has obtained its maximum temperature of 359 degrees Kelvin in
approximately 445 seconds. The reaction was the fastest among three experiments involving the foam reaction. Slightly higher initial temperature of the foam was likely to be the factor in accelerating the reaction. A temperature behavior of a mold has also come out to be very similar to that of the Figure 2, with approximately 6 degrees Kelvin increase.
In this chapter, the temperature of the polymer containing isocyanate and polyol is considered. A method known as an adiabatic method was directly applied to the experimental data in order to find the reaction kinetics. Two common overall cure kinetic models known as an “n-th order model” and an “autocatalytic model” were used in order to predict the temperature history of the foam during the curing process. Also, the effect of heat transfer, which takes place after the completion of the chemical reaction was studied using a simplified energy balance equation.

3.1 Brief Review of the Adiabatic Method

The adiabatic method has been widely used by several investigators as an indirect method for measuring the reaction kinetics. Fast reacting exothermic systems, such as those used in the reaction injection molding, are usually analyzed as adiabatic or nearly adiabatic systems, and their reaction kinetics can be studied using the indirect method. Camargo [Camargo, 1982, 1984] and Macosko [Macosko, 1989] have conducted many experiments using polypropylene cup and thermocouples to measure the temperature of the polymer reactant inside the cup. In many cases, the temperature history of the reactant obtained from the experiment was in very good agreement with that obtained by the adiabatic method.

The foam used in this experiment is an isocyanurate, in which polyol and isocyanate are reacted to form a primarily crosslinked polyurethane and a cyanurate
trimer. In this study, the temperature of the foam was measured as a function of time during the curing process. The kinetic model is then deduced from those temperature measurements. It is known that for the system with a rapid and highly exothermic reaction, an assumption of the system to be in an adiabatic condition is valid, knowing that the polymer conductivity is low [Camargo, 1984] and [Macosko, 1989]. In the experiment, it was possible to assume that the reaction is highly exothermic and moderately fast, with approximately 400 seconds until the maximum exothermic temperature was achieved, i.e., a completion of the reaction. Therefore, the preliminary chemical kinetics analysis of the foam was based on the adiabatic method, in which a temperature history was related to a reaction variable through an energy balance equation. The equation of conservation of energy, with the assumption of a homogeneous reaction, no heat losses, and no diffusion effects, is:

\[ C_p \frac{dT}{dt} = -(\Delta H) C_0 \frac{dx}{dt} \]

Here \( x \) is the fractional monomer conversion, \( C_p \) is the heat capacity per unit volume in J/liter\(^\circ\)K, \( -(\Delta H) \) is the heat of reaction in J/liter, and \( C_0 \) is the initial concentration of the isocyanate [Camargo, 1984]. Eliminating \( dt \) in Eq.(1) and integrating, results in a relation between \( x \) and the temperature \( T \). With the common assumption of a constant \( -(\Delta H) \), taken as an average value of the heat of reaction, as well as a constant \( C_p \), \( x \) can be defined as:

\[ x = \frac{\frac{T - T_{inital}}{T_{final} - T_{inital}}}{\frac{T_f - T_0}{T_f - T_0}} \]

This definition of \( x \) was directly used in the common overall cure kinetic models known as “n-th order” and “autocatalytic” as defined by [Camargo, 1984] as:
\[
\frac{dx}{dt} = A \exp\left(\frac{-E}{T}\right)(1-x)^n
\]

(3)

\[
\frac{dx}{dt} = A \exp\left(\frac{-E}{T}\right)(1-x)^n (1 + B_0 x)
\]

(4)

where \(x\) is a fractional monomer conversion, \(n\) is the reaction order, which measures the slow down of the reaction due to reactant consumption, \(E\) is defined as \(E_a/R\) having units of degrees Kelvin, and \(B_0\) is the autocatalysis intensity, which measures any acceleration of the rate of reaction that takes place due to effects other than temperature.

3.2 Application of the Method to Experimental Data

In order to determine the kinetic parameters, \(A\), \(E\), and \(n\) for the \(n\)-th order model, or, similarly, \(A\), \(E\), \(n\), and \(B_0\) for the autocatalytic model, three or four nonlinear equations were set up using experimental data for the foam temperature. Small fluctuations of the experimental data were smoothed by approximating the experimental results by a best-fitting polynomial, using a least-squares approximation method. Figure 6 shows both the experimental data and the best fitting polynomial. Since the agreement between the experimental data and the approximating polynomial is good, the difference between the two curves is hardly distinguishable, except at the initial and at the maximum temperatures. Here, a solid line indicates the experimental data, while circles show two best-fitting polynomials for the reaction and the heat loss segments combined. Figure 7 shows the temperature history during the reaction for a time interval during which the temperature varies from the initial value until it reaches a maximum. The fifth-degree polynomial shown by the solid line approximates the experimental data shown by stars. Figure 8 shows the values of the derivative \(dT/dt\) as obtained directly from the experimental data using a finite difference approximation (stars) and as computed from the polynomial representation (solid line). In order to eliminate the temperature fluctuations obtained in the experiment, several values of the time step \(\Delta t\) were tried in
the estimation of the derivative $dT/dt = \Delta T/\Delta t$, however, better results (smoother curve) were obtained using the polynomial approximation.

Eqs.(2-4) were substituted into Eq.(1). Assumption of having an average heat of reaction and constant heat capacity allows those constants to cancel out at the end, leaving the following expressions for the two kinetic models:

\begin{align}
(5) \quad \frac{dT}{dt} &= (T_f - T_0)A \exp\left(\frac{-E}{T}\right)\left(\frac{T_f - T}{T_f - T_0}\right)^n \\
(6) \quad \frac{dT}{dt} &= (T_f - T_0)A \exp\left(\frac{-E}{T}\right)\left(\frac{T_f - T}{T_f - T_0}\right)^n \left(1 + B_0\frac{T - T_0}{T_f - T_0}\right)
\end{align}
where $T_f=225^\circ F$ (380$^\circ K$) and $T_0=72^\circ F$ (295$^\circ K$) are known experimentally. Derivations of these equations are discussed in more detail by [Camargo, 1984]. Since there were no experimental data available for $dx/dt$ (which can otherwise be measured directly by differential scanning calorimeter), it was assumed that the reaction went to completion (i.e. $x=1$ and $dx/dt=0$) when the temperature reached a maximum, according to Eqs.(1-6). Substituting Eqs.(2) and (3) into Eqs.(5), or Eqs.(2) and (4) in Eq.(6), the rate of change of temperature is obtained as a function of the reaction rate as follows:

\[
(7) \quad \frac{dT}{dt} = (T_f - T_0) \frac{dx}{dt}
\]

Therefore, $dx/dt$ approaches zero when the rate of change of the temperature, $dT/dt$, also approaches zero. This occurs when $T=T_{\text{max}}$ as shown in Figure 9, resulting in completion of the reaction at the maximum temperature. Because of this assumption, the energy
balance of Eq.(1) was directly applied assuming that there was no heat loss prior to reaching $T_{\text{max}}$.

![Figure 9: Rate of Reaction vs Time of Foam during Reaction](image)

3.3 Numerical Method

Three or four sets of temperature and its corresponding derivative from Figures 7 and 8 were then substituted in Eqs.(5-6). These values of the temperature and its derivative were chosen for their good distributions along the curve of the best-fitting polynomial. However, due to its inaccurate representation of the experimental data at the extremities of the time interval $t_0$ to $t_f$, the first and last 100 seconds of the time series data were disregarded. The systems of nonlinear algebraic equations were then solved by an iterative method using initial guesses of $A$, $E$, $n$, and $B_0$, and Gauss-Newton method. Using the experimental results at a finite number of points and writing the kinetic
equations at the chosen points the following systems of nonlinear algebraic equations are obtained for the n-th order and the autocatalytic models, respectively:

\[
(8) \quad \left( \frac{dT_i}{dt} \right)_i - (T_f - T_0) A \exp \left( \frac{-E}{T_i} \right) \left( \frac{T_i - T_f}{T_f - T_0} \right)^n = 0 \quad ; \quad i=1,2,3
\]

\[
(9) \quad \left( \frac{dT_i}{dt} \right)_i - (T_f - T_0) A \exp \left( \frac{-E}{T_i} \right) \left( \frac{T_i - T_f}{T_f - T_0} \right)^n \left( 1 + B_0 \frac{T_i - T_0}{T_f - T_0} \right) = 0 \quad ; \quad i=1,\ldots,4
\]

where \( T_i \) and \( (dT/dt)_i \) correspond to different experimental values of \( T \) and \( dT/dt \) chosen as different points along the curves of Figures 7 and 8. Depending on the type of kinetic model used, three or four experimental points are used to form three or four algebraic equations. Three experimental points are used to solve for the three unknown parameters \( A, E, \) and \( n \). Four experimental points are needed in order to solve for the four parameters \( A, E, n, \) and \( B_0 \). The number of equations in each case was kept minimum to number of unknowns in order to obtain the better convergence of solutions and minimize errors to the equations.

Since an iterative method is used to determine the kinetic parameters, it is desirable to start the iteration with reasonable values of the unknowns. The initial values of the unknown parameters \( A, E, \) and \( n \) were found using an independent simplified parameter determination method, which is based on the n-th order kinetic model. Such a simplified method for determining the activation energy was proposed by [Macosko, 1989]. It uses the maximum temperature \( T_{\text{max}} \), the temperature \( T_{\text{mr}} \) at which the maximum slope \( (dT/dt)_{\text{max}} \) occurs, and the reaction order \( n \). \( B_0 \) was initially assumed to be zero. An approximate value for the activation energy is then given by:

\[
(10) \quad E = \frac{nT_{\text{mr}}^2}{T_{\text{max}} - T_{\text{mr}}} = \frac{E_a}{R}
\]
where the following values were obtained experimentally from Figures 7 and 8:

\[ T_{mr} = 115^\circ F = 319^\circ K \] at \((dT/dt)_{\text{max}} = 0.427^\circ K/s\)

\[ T_{\text{max}} = 225^\circ F = 380^\circ K \]

Here \(E_a\) is the activation energy and \(R\) is the universal gas constant. The simplified parameter determination mentioned above is described in greater detail by [Macosko, 1989] and [Camargo, 1984]. With an approximate value of \(E\) obtained from Eq.(10), with \(n\) varying from 0 to 2 at the increment of 0.1, the parameter \(A\) was determined using the \(n\)-th order kinetic model of Eq.(5). Typical value of \(n\) for the foam is known to be 2. \(T_f\) and \(T_0\) to be substituted into Eq.(5) are known from the experimental data as explained previously. For the \(n\)-th order model, it was found that the iterative solution always converges to the same values of kinetic parameters, regardless of the initial values used.

Using the method described above, the foam was found to have the following values for the kinetic parameters. Eq.(5) can then be rewritten as:

\[
\frac{dT}{dt} = (T_f - T_0)A \exp\left(-\frac{E}{T}\right)\left(\frac{T_f - T}{T_f - T_0}\right)^n
\]

\[ A = 1.8162s^{-1} \]
\[ E = 1792.5K \]
\[ n = 1.0377 \]

where \(T_f\) and \(T_0\) are as defined previously. Eq.(11) describes the \(n\)-th order chemical kinetic model of the foam used in the experiment. It was found that these chemical kinetic parameters are comparable to the values found by the simplified parameter determination with a value of \(n\) around 1.06. However, a minimization of \(\Delta T\) between the experimental data and the theoretical model was most successful with the parameter set given by Eq.(11). Figure 10 shows the result of solving the differential equation, Eq.(11), which is shown by the solid line. A polynomial representation of the experimental data points are shown by stars. It is important to note at this point that only the curve between the initial and final (maximum) temperature was considered, since the determination of chemical kinetic parameters requires only the temperature history during
the reaction be known. The effect of heat transfer, which starts after the completion of the reaction, will be discussed later, and the combined effects of the chemical reaction and the heat transfer will be presented graphically.

![Chemical Kinetics Representation of foam by an Adiabatic Method (n-th order)](image)

For the autocatalytic model, the iterative method converged to the same solution when started from different initial values, despite the crude assumption of an initial value of zero for the parameter $B_0$. Consequently, the foam was found to have the following values for the kinetic parameters, and Eq.(6) can then be written as:

\[
\frac{dT}{dt} = (T_f - T_0)A \exp\left(\frac{-E}{T'}\right)\left(1 + B_0\left(\frac{T - T_0}{T_f - T_0}\right)\right)
\]
\[ A = 13.56 \text{s}^{-1} \]
\[ E = 2393 \text{K} \]
\[ B_0 = -0.9152 \]
\[ n = 0.4529 \]

Figure 11 shows the result of solving Eq.(12), which is given by the solid line. The polynomial approximation of the experimental points are represented by stars. At a first glance, it is difficult to distinguish the difference between the results of the n-th order and the autocatalytic models shown in Figures 10 and 11. However, when the sum of the squares of the differences were calculated for the set of non-linear equations, it was found that an autocatalytic model had a much smaller error. It was possible to obtain many combinations of the kinetic parameters which result in similar behavior to that of the experimental data. Therefore, it was necessary to optimize the solution by choosing a set of kinetic parameters which yields the smallest error among all the other possible sets. For this reason, it was concluded that autocatalytic chemical kinetic model of Eq.(12) represents the temperature profile of the foam being used in this experiment with a minimum error.
3.4 Possible Errors in the Solution

Major source of error in this analysis was the use of a best-fitting polynomial, instead of the experimental data itself. This may have introduced a large error where the fitting between the polynomial and the experimental data was poor. It should be mentioned that the higher degrees of polynomial with an excellent agreement with the experimental data was also studied. However, it was found that those higher order polynomials yield hardly converging solutions for the given nonlinear equations. Eventhough the convergence was achieved after many iterations, the kinetic parameters obtained from this process was found to yield an undesired temperature profiles. It was also difficult to choose the time interval to be disregarded for the poor fittings. Although these intervals were visually chosen from Figure 7 to be first and last 100 seconds, it was found that even a small change in the time interval may largely influence the kinetic parameters, A, E, n, and B₀. Also, changing the number of points to be used in the optimization of a set of nonlinear equations have somewhat influenced the values of the kinetic parameters. However, it was observed that the least-square error between the experimental data and analytical temperature profile seemed to have increased with increasing number of points. For those reasons, mechanistic interpretations of these parameters are not recommended, since this variation of parameters may be an indication that a different kinetic mechanism existed before and after the gel point, and thermal properties, ρ and Cₚ may not have been constant in the whole cure, according to Lee and Macosko [Lee, 1980].

3.5 The Effect of Heat Transfer

A rapid heat loss starts to take place as soon as the mixture reaches the completion of a reaction. An energy balance equation for this state is defined by Lee and Macosko [Lee, 1980] as:

\[ C_p \frac{dT}{dt} = -h^*(T - T_a) \]
where $C_{pu}$ is the heat capacity at constant pressure of the urethane foam in cal/(g°K), $h^*$ is the modified heat transfer coefficient in cal/(g sec °K), defined by:

$$h^* = \frac{hA}{M}$$

where $h$ is the heat transfer coefficient in cal/(°K cm² sec), $A$ is the heat transfer area in cm², and $M$ is the mass of a reacting mixture in grams. $T_a$ is an ambient temperature in degrees Kelvin. The experimental time series for the temperature displayed fluctuations due to noise in the system and in the data acquisition equipment. The heat loss segment of the time series was smoothed by employing the best-fitting polynomial, and the result is shown as Figure 12. A 13th degree polynomial is used for smooth approximation of the experimental data. As can be seen from the figure, with solid line representing the
polynomial of an experimental data in stars, the approximation is very good. Figure 13 shows the derivatives for both experiment and its polynomial representation. The dotted line shows dT/dt for the experiment, while solid line represents the derivative as computed from the data smoothing polynomial approximation. The fluctuations measured in the experiment are completely eliminated. Although hardly noticeable from the graph, it was observed that the data from the polynomial for the last few hundred seconds was obviously not fitting that of the experiment, and was discarded in subsequent calculations. A set of T and dT/dt from Figures 12 and 13 was substituted in Eq.(13). Since \( T_a = 81.2^\circ F (300.48^\circ K) \), a corresponding value of \( h^*/C_{pu} \) was calculated for each time step. The result is shown in Figure 14. It can be seen that the value of \( h^*/C_{pu} \) increases toward the end as the difference between the temperature at a given time and the ambient temperature decreases. A time interval of the last 280 seconds was chosen to be discarded for its inaccurate representation of the experimental data, as it can be seen from Figure 14. Assuming \( C_{pu} \) to be constant, average value of \( h^*/C_{pu} \) was determined from Figure 14 in order to simplify the problem. However, since it was difficult to determine where to cut the data points off for their inaccurate fittings to the experimental data, a least-square error was found between the best-fitting polynomial and the result of
solving a differential equation of Eq.(13), each time a certain amount of data points were being deleted and new average $h^*/C_{pu}$ was determined and substituted into Eq.(13). The value of $h^*/C_{pu}$, for which the least-square error was obtained, was chosen as the final value. After a few trials, a trend of change in $h^*/C_{pu}$ and the least-square error for the result became clearly understood, and the final average $h^*/C_{pu}$ was easily determined to be $9.5309 \times 10^{-4}$ s$^{-1}$, after deleting 280 seconds of data at the end. The result of solving Eq.(13), with this average $h^*/C_{pu}$ is shown in Figure 15. A solid line represents that for the Eq.(13), while stars show the best-fitting polynomial to the experimental data. Slight errors between the two curves are likely to be the result of having an average value of $h^*/C_{pu}$. Also, using the polynomial approximation instead of the experimental data itself has produced an error between the two curves, which eventually lead the calculation to proceed by deleting part of the data. A solid line in Figure 16 shows the final result of combining the theoretical models of chemical kinetics and heat transfer for the foam.
being studied in this experiment, along with the polynomial representation of an experimental data shown by stars.

Figure 16 Theoretical and Experimental Temperature Profiles of Foam

solid line=theoretical model
star=polynomial
In this chapter, a curing of the general purpose resin was considered. However, because of the limited available experimental data, many assumptions were made in order to study the material. Among these are the use of the basic definition of a heat, in which only available experimental data of temperature history was directly related to the amount of heat generation by the resin. This procedure has given an isothermal degree of cure and its derivative at a given time. A nonlinear least-squares curve fit to these values was used to find the kinetic constants in the theoretical model. The results of integrating this model was compared to the experimental degree of cure as well as to the raw data of temperature profile.

4.1 Isothermal Degree of Cure

In recent years, analytical model has been proven to be successful in selecting an appropriate temperatures and pressures for the curing of organic matrix composites. An equipment called a differential scanning calorimeter (DSC) has been widely used to generate the data for the degree of cure, the rate of cure, and the heat of reaction. In this technique, a small sample is heated at a constant rate (dynamic scanning) or to a particular temperature (isothermal scanning) and the heat flow to or from the material is monitored [White, 1991]. An exothermic flow of heat by the crosslinking reaction in thermosetting polymers and the characterization of the cure state can specifically be monitored by the DSC. In our experiment, temperature profile of the resin was the only
available measurement, and many assumptions were needed in order to study the cure kinetics of the polymer. First, the temperature history of the resin had to be related to the amount of heat being produced by the reaction. The isothermal degree of cure, \( \beta \), is defined as the ratio of the amount of heat release in time \( t \), to the isothermal heat of reaction [Springer, 1987]:

\[
\beta = \frac{1}{H_T} \int_0^t \left( \frac{dQ}{dt} \right)_T \, dt
\]

where \( H_T \) is the isothermal heat of reaction in Joule, defined by the following integral:

\[
H_T = \int_0^{t_n} \left( \frac{dQ}{dt} \right)_T \, dt
\]

where \( t_n \) is the time at which no more heat generation can be observed at the constant temperature of the experiment. In both Eq.(15) and Eq.(16), \( (dQ/dt)_T \) is the instantaneous rate of heat generation at isothermal condition. However, unlike direct DSC measurement of heat generations, a definition of heat involving a resin temperature had to be used for our experiment in order to determine the isothermal degree of cure, \( \beta \), at a given time. This was done by using the basic definition of heat given by [Young, 1992] as:

\[
Q = mc\Delta T
\]

where \( m \) is the mass in kg, \( c \) is the specific heat capacity in J/(kg °K), and \( \Delta T \) is the temperature difference, \( T_2 - T_1 \) in degrees Kelvin. This definition implies that the amount of heat \( Q \), required to raise the temperature of a material from \( T_1 \) to \( T_2 \) depends on the mass and the characteristics of a material, and the temperature difference during the time of an interest. In determining \( H_T \) and \( (dQ/dt)_T \), it was assumed that the surrounding temperature of the resin, the room temperature in our case, was constant. This assumption was made so that the definition of isothermal heat of reaction and the rate of
heat generation for the DSC experiment is also applicable to our experiment. Past experience with the DSC technique shows that an isothermal condition (constant ambient temperature) was to be maintained when determining the thermal characteristics of the resin. The heat generated after a time \( t \) can then be obtained from Eq.(17), or by integrating the rate of heat \((dQ/dt)_T\) generated at constant ambient temperature:

\[
Q = \int_0^t \left( \frac{dQ}{dt} \right)_T dt = mc(T - T_0)
\]

where \( T \) is the temperature at a given time and \( T_0 \) is the initial temperature, which are known experimentally. Temperature is in degrees Kelvin.

The isothermal heat of reaction \( H_T \) can be defined in a similar manner. \( H_T \) is the total heat generated from \( t=0 \) until the chemical reaction has been completed at a constant ambient temperature:

\[
H_T = mc(T_f - T_0)
\]

where \( T_f \) and \( T_0 \) are the maximum and initial reacting temperatures from the experiment. Assuming a constant specific heat capacity, the isothermal degree of cure of the resin can be obtained from Eqs.(18-19):

\[
\beta = \frac{Q}{H_T} = \frac{T - T_0}{T_f - T_0}
\]

A maximum \( \beta \) of unity indicates the isothermal completion of the reaction. With this definition of \( \beta \) and its corresponding derivative \( d\beta/dt \), found by the numerical method, a theoretical kinetic model of the resin was considered. According to many researchers, the isothermal degree and rate of cure of resin are related by the following expression:
where $m$ and $n$ are the constants describing the order of the reaction, and are independent of the temperature. $K_1$ and $K_2$ are reaction rate constants, which depend on the temperature according to the relations:

$$
\begin{align*}
K_1 &= A_1 \exp(-\Delta E_1 / RT) \\
K_2 &= A_2 \exp(-\Delta E_2 / RT)
\end{align*}
$$

where $A_1$ and $A_2$ are the pre-exponential factors, $\Delta E_1$ and $\Delta E_2$ are the activation energies, $R$ is the universal gas constant, and $T$ is the curing temperature (room temperature in our experiment) in degrees Kelvin [Springer, 1987].

4.2 Application of the Analysis to Experimental Data and the Numerical Analysis

In analyzing our experimental data, a best-fitting polynomial using a least-square method was first found, in order to minimize the fluctuations in the data. Figure 17 shows the polynomial as the solid line, successfully representing the fluctuating experimental data shown by the stars. The next step was to extract the reacting segment (i.e. a temperature data during the reaction) from Figure 17 to be used in the numerical analysis. This was done by assuming that there was no reaction for the first 5400 seconds, or 90 minutes. Since the experiment was done in the room temperature, it was observed that the resin did not start reacting right away, due to its low surrounding temperature. The resin was in thermal equilibrium with the environment at the ambient temperature for the first one hour and thirty minutes before the reaction started. Therefore, a temperature data between $t=5400$ seconds to 10800 seconds, in which resin attains the maximum temperature, was taken to be the reacting segment. Using these temperature data, an isothermal degree of cure, $\beta$, at a given time was obtained from Eq.(20), with $T_0=294.45^\circ K$ and $T_f=300.094^\circ K$. The result is shown in Figure 18, in which $\beta$ starts from
zero and approaches unity, as the isothermal completion of the reaction is being achieved. Figure 19 shows the $d\beta/dt$ obtained by the numerical method, and it was observed that the maximum rate of cure occurs around 0.5 degrees of cure, or 50% reaction completion. Four sets of $\beta$ and its corresponding $d\beta/dt$, chosen for their good distributions along the curves, were taken from Figures 18 and 19 to be used in the nonlinear least-squares curve fit to Figures 17 and 18. Using Eq. (21), a following format was used in order to solve for four unknowns, $m$, $n$, $K_1$, and $K_2$, using four sets of $\beta$ and $d\beta/dt$:

\[
\left( \frac{d\beta}{dt} \right) - \left( K_1 + K_2 \beta^n \right) (1 - \beta)^m = 0 ; \quad i = 1, \ldots, 4
\]

The number of equations was kept minimum to number of unknowns in order to obtain the better convergence of solutions and minimum errors to the equations. A computer program that employs a Gauss-Newton algorithm was written, with initial values of
kinetic parameters taken from the research work on various resin systems done by Mallick [Mallick, 1993]. A convergence of solutions was fast and consistent in a way, that all of the initial values of kinetic parameters from the literature have converged to one set of solutions. For our resin, it was determined that $K_1=5.7507e^{-7}s^{-1}$, $K_2=8.3865e^{-4}s^{-1}$, $m=0.6491$, and $n=0.6415$. Substituting these values into Eq.(21) yields following expressions for $d\beta/dt$:

$$\frac{d\beta}{dt} = (K_1 + K_2\beta^m)(1 - \beta)^n$$

$K_1=5.7507e^{-7}s^{-1}$
$K_2=8.3865e^{-4}s^{-1}$
$m=0.6491$
$n=0.6415$

A result of integrating Eq.(24) is shown by the solid line in Figure.20, while stars represent the experimental $\beta$, using Eq.(20). Although there was a numerical problem in
Figure 20 Experimental and Theoretical Isothermal Degree of Cure, Beta of Resin vs Time

Figure 21 Experimental and Theoretical Temperature Profile of Resin
solving Eq.(24), in which some $\beta$ contained imaginary numbers, a theoretical model has
given a good agreement with the experimental isothermal degree of cure. Figure.21
shows the theoretical temperature found from Eq.(20), by solving for $T$ at a given $\beta$ from
Eq.(24). Again, a theoretical model in a solid line has given a good agreement with the
experimental data in stars. No significant errors seemed to have occurred in this analysis,
because of the good agreement between the best-fitting polynomial and the experimental
data at the segment where the data was taken for the numerical analysis.
In this chapter, the interaction between the polyurethane foam and the resin will be considered. A preliminary cure model for the resin will be introduced in order to explain the process of analyzing the interaction. However, due to lack of several experimental data, it was not possible to study the material in depth, or to validate the model. Therefore, the final result of the polyurethane foam and resin interaction will not be presented in this thesis.

5.1 Discussion of the Resin Temperature Profile

The temperature histories of a polyurethane foam and resin were studied individually in two previous chapters. In this chapter, the combined temperature effects of these two materials are considered, when the resin is in a curing stage. First, a temperature profile of a sole reaction of the resin is repeated in figure 22, in order to clarify the temperature behavior of the resin. Here, the temperature data for the bottom resin was omitted, for the profile was very similar to that of the top resin. It can be observed that the reaction is taking as much as 6000 seconds, or one hour and forty minutes without any external heat to speed up the reaction. Also, the temperature increase of the resin was only about 5 degrees Kelvin. However, as it may be observed in figure 23, when the foam was applied to the resin in a gelled curing stage, the resin has received some heat from the rapid and highly exothermic reaction of a foam. As a result, the reaction of a resin was considerably faster and more stable. In chapter 2, it was mentioned that only 2000
seconds were needed to attain the maximum temperature, however, this does not necessarily mean that the reaction was taking 2000 seconds. As it may be observed
in figure 23, there is an obvious change in the rate of temperature increase of resin around 320 seconds. It is not possible to determine whether this point or the point at the maximum temperature around 2000 seconds is the completion of a reaction, since the only available experimental data is the temperature profile. DSC (differential scanning calorimeter) is necessary in order to determine whether the reaction has completed or not, since the equipment is capable of measuring the degree and the rate of cure of the resin. However, it is possible to consider that the temperature around 320 seconds is the maximum exothermic temperature, i.e., a completion of the reaction. An additional 25 degrees Kelvin increase of a resin, as shown in figure 23, may have come from the heat transfer of the foam. As it may be observed in figure 24, a completely cured resin can increase its own temperature up to 15 degrees Kelvin just from the reaction heat of a foam.

Very similar behavior may be observed for the case of a resin in the wet curing stage, as shown in figure 25. For this experiment, there is an apparent change in the rate of temperature increase around 400 seconds. A temperature rather decreases for next 1100
seconds, until it starts increasing again around 1500 seconds. Also for this experiment, it is possible to assume that the reaction has completed around 400 seconds and an additional temperature increase of 22 degrees Kelvin may have come from the foam reaction. However, because of its uncertainty, it is safe to say that the points of the reaction completion for both gelled and wet curing stages remain undetermined from the given experimental data. In a word, it is recommended that the DSC measurements be taken in order to determine the point of a reaction completion. This process is expected to simplify the analysis of the interaction between the polyurethane foam and the resin.

5.2 Discussion of the Resin Cure Model
Prior to the discussion of a proposed theoretical model of an interaction between the polyurethane foam and the resin, a missing information about the resin kinetics should be mentioned. As it was discussed in chapter 4, an isothermal degree and rate of cure of our resin were related by the following expression:
\[
\frac{d\beta}{dt} = (K_1 + K_2 \beta^m)(1 - \beta)^n
\]

\[K_1 = 5.7507 \times 10^{-7} \text{s}^{-1}\]
\[K_2 = 8.3865 \times 10^{-4} \text{s}^{-1}\]
\[m = 0.6491\]
\[n = 0.6415\]

The kinetic constants, \(K_1\), \(K_2\), \(m\), and \(n\) found by the nonlinear least-squares curve fit, were enough information needed to represent the curing model of the resin at a particular temperature, where the experiment was performed. An integration of Eq.(25) has yielded a result as shown in Figure 20, validating the cure model and its constants at this particular temperature. However, \(K_1\) and \(K_2\), known as reaction rate constants, strongly depend on the temperature as follows:

\[
K_1 = A_1 \exp(-\Delta E_1 / RT)
\]
\[
K_2 = A_2 \exp(-\Delta E_2 / RT)
\]

where \(A_1\) and \(A_2\) are the pre-exponential factors, \(\Delta E_1\) and \(\Delta E_2\) are the activation energies, \(R\) is the universal gas constant, and \(T\) is the curing temperature (room temperature in our experiment) in degrees Kelvin, as discussed in chapter 4. Therefore, \(K_1\) and \(K_2\) are expected to change for a different surrounding temperature. In a word, the constants in the isothermal degree and rate of cure model, Eq.(25), for a given resin are, \(A_1\), \(A_2\), \(\Delta E_1\), and \(\Delta E_2\). Once these constants are obtained, the curing process at different temperatures may be determined by substituting the curing temperature in Eq.(26) and then Eq.(25).

It should be mentioned that the nonlinear least squares curve fit was attempted in order to find four unknowns, \(A_1\), \(A_2\), \(\Delta E_1\), and \(\Delta E_2\), using the experimental data. This was done by using four points and \(m\) and \(n\) values found by the previous analysis, knowing that they are not the functions of a cure temperature. However, because of the exponential terms, solutions were highly unstable, and no appropriate set of kinetic parameters were obtained by matlab. In order to find the kinetic constants \(A_1\), \(A_2\), \(\Delta E_1\), and \(\Delta E_2\) properly, it is necessary to obtain a few more reacting temperature profiles of a resin at a different
curing temperature, that is kept constant (i.e. isothermal) throughout the entire experiment. The activation energies and pre-exponential factors can be obtained by plotting the natural logarithm of $K_1$ and $K_2$ from several different isothermal experiments, versus the inverse of their corresponding cure temperatures. The resulting plot should give a straight line with a slope of $-\Delta E/R$ and an intercept $\ln(A)$ [White, 1991]. Once $A_1$, $A_2$, $\Delta E_1$, and $\Delta E_2$ are determined from this procedure, any curing temperature may be substituted into Eq.(27) as follows, and the temperature behavior of the resin may be studied in depth.

\[
\frac{dB}{dt} = (A_1 \exp(-\Delta E_1 / RT) + A_2 \exp(-\Delta E_2 / RT)\beta^n)(1 - \beta)^n
\]

This process will also validate the curing model for this particular resin, since the integration of Eq.(27) may be compared to several experimental data at various cure temperatures, by relating $\beta$ to the temperature at a given time, as discussed in chapter 4.

### 5.3 Proposed Theoretical Model of Polyurethane Foam and Resin Interaction

An appropriate approach to analyze the interaction between the polyurethane foam and the resin is to set up the equation for each material, that defines the individual temperature variation during the interaction. These equations are coupled, or dependent on one another. The law of conservation of energy together with an appropriate expression for the cure kinetics is used in order to calculate the temperature inside the resin as described by [Hou, 1987] and [Mallick, 1990] as;

\[
\rho_r C_r \frac{\partial T_r}{\partial t} = K_r \frac{\partial^2 T_r}{\partial y^2} + \rho_r H_r f(\beta)
\]
and the foam as described by [Vespoli, 1985]:

\[
\rho_f C_f \frac{\partial T_f}{\partial t} = K_f \frac{\partial^2 T_f}{\partial y^2} + \rho_f H_f f(x)
\]

(29) \[\rho_f C_f \frac{\partial T_f}{\partial t} = K_f \frac{\partial^2 T_f}{\partial y^2} + \rho_f H_f f(x)\]

\[\rho\] is the density in kg/m³, \(C\) is the specific heat in J/kg.K, \(K\) is the thermal conductivity in the direction perpendicular to the plane of composite material in watt/m.K, and \(H\) is the specific ultimate heat of reaction in J/kg, for each material. \(f(\beta)\) and \(f(x)\) are the expressions for the resin and the foam cure models. For both equations, the first term on the right hand side deals with the heat transmitted by conduction from the surrounding environment, while the second term is dealing with the heat generated by the reaction, with the cure kinetic models of the resin and the foam. The heat transferred by convection is neglected in most cases. Each term in Eq.(28) and Eq.(29) represents the rate of internal or volumetric heat generation in watt/m³.

Following drawing shows the side view of our composite material for the clarification purpose:

FIGURE 26. Side view of the composite material
Here, the initial conditions are:

(30) \( t=0; \quad T_{\text{foam}}=T_{\text{resin}}=T_{\text{ambient}}, \quad T(y)=T_{\text{ambient}} \)

The boundary conditions are:

(31) \( y=b+h; \quad T(b+h)=T_{\text{ambient}} \)
(32) \( y=b; \quad T_i(b)=T_i(b) \)
(33) \( y=b; \quad K_r \frac{dT_r}{dy}(b) = K_f \frac{dT_f}{dy}(b) \)
(34) \( y=0; \quad \frac{dT_f}{dy}(0) = 0 \)

At \( y=b, \ T=T_b, \) and at \( y=b+h, \ T=T_{\text{ambient}} \) as it is shown in figure 26. Eq.(32) and Eq.(33) comes from imposing the conditions of continuity of temperature and continuity of the normal component of the heat flux vector, \( q \cdot n. \) These conditions are given under the assumption that the foam and the resin are continuous at the interface, i.e., there is no air gap at the interface as described by [Whitaker, 1977]. Eq.(34) comes from the symmetry of the material.

However, this method was not studied in this thesis because of its time-consuming nature, as well as the difficulty in applying it to the existing experimental results. In order to simplify the problem and to utilize the experimental data in the analysis, an approximate method known as the heat-balance integral method (HBIM) was considered. Although the result of applying this method will not be presented here, the procedure and the trial used to analyze the problem will be discussed.

The heat-balance integral method has been widely used by many investigators in order to study the transient heat-conduction problems. This method is based on the concept that the solution of one-dimensional, time-dependent boundary value problems of heat conduction will satisfy the problem not at every differential element in the region but only on the average over the region considered. The advantage of heat-balance integral
method is that the associated mathematical procedure is fairly straightforward, eventhough it is capable of handling the complicated boundary conditions, such as the nonlinear heat flux. Despite of being an approximation method, the accuracy of heat-balance integral method was confirmed to be acceptable for engineering purposes. The details of this method is described by [Ozisik, 1968].

First, the following figure is provided for the purpose of clarifying the heat-balance integral method being applied to our composite material.

FIGURE. 27 Cross-section of the composite material for heat-balance integral method

Here, the bottom portion was omitted for it was assumed to have the same temperature variation, due to its symmetry as shown in figure 26.

The resin is initially at room temperature $T_r$. For time $t>0$, a chemical reaction generates the heat at a rate of $g(t)$ in watt/m$^3$, while the boundary at $y=0$ has nonlinearly changing temperature from polyurethane foam reaction. This boundary-value problem of heat conduction is defined as:

$$
\frac{\partial^2 T}{\partial y^2} + \frac{g(t)}{K} = \frac{1}{\alpha} \frac{\partial T}{\partial t} \\
0 \leq y < h, \; t > 0
$$

Here, $K$ is the thermal conductivity in W/m-K, $\alpha$ is the thermal diffusivity in m$^2$/s, which can also be expressed as $K/\rho C_p$. In heat-balance integral method, the phenomenological distance $\delta(t)$, known as the thermal layer thickness, takes the major
role. The thermal layer in the heat-conduction problem is defined as the distance from the origin beyond which the initial temperature distribution within the region remains unaffected by the applied boundary condition, and therefore there is no heat flow beyond $\delta(t)$. It is important to be mentioned here that the separate procedures are needed to analyze the finite and infinite heat conduction problem however, the treatment of two problems are the same as long as the thermal layer thickness $\delta(t)$ is less than the thickness of the region, $h$, in figure 27. As soon as $\delta(t)$ exceeds $h$, thermal layer has no physical significance and additional treatment will be needed. However, in this analysis, $\delta(t)$ was treated to be equal to $h$, so as to simplify the calculation. It has to be mentioned here, that the several trials using HBIM were performed using different sets of boundary conditions. However, it was determined that many assumptions or simplifications were needed in order to make the problem analytical. As a result, $\delta(t)$ was assumed to be $h$, the thickness of the resin. At the same time, two boundary conditions and one initial condition were considered:

$$T(0,t) = T_f(t) \quad \text{where} \quad T_f(t) = T_{foam}$$

(37) \[ \left. \frac{\partial T}{\partial y} \right|_{y=h} = 0 \]

(38) \[ T(y,0) = T_o \]

Equation (36) states that at the boundary of $y=0$, the temperature is always that of the polyurethane foam at all times. Equation (37) comes from an assumption of having an adiabatic mold. Initial condition of Equation (38) states that the temperature of the composite material is the same as the ambient temperature at $t=0$.

The next step is to assume a temperature profile of the second-order polynomial or the parabola, that defines the temperature distribution inside the resin. The
use of the polynomial is one of the assumptions in the heat-balance integral method, which is commonly used to simplify the calculation.

\[ T(y,t) = A + By + Cy^2 \]

Here, A, B, and C, are the coefficients, and y is the any location inside the resin, as it is shown in Figure 27.

There is one more equation needed to solve for the three coefficients in Equation (39), along with two boundary conditions defined previously. For this purpose, a heat-balance equation for the problem involving a heat generation is considered. An equation (35) can be integrated from y=0 to y=h for the application to our problem. A similar result was derived by [Ozisik, 1968] in terms of the thermal layer thickness, \( \delta(t) \). In terms of the resin height, h, the heat-balance equation becomes:

\[
\frac{\partial T}{\partial y} \bigg|_{y=h} - \frac{\partial T}{\partial y} \bigg|_{y=0} + \int_{y=0}^{h} \frac{g(t)}{k} \, dy = \frac{1}{\alpha} \left[ \frac{\partial}{\partial t} \int_{y=0}^{h} T \, dy - \frac{dh}{dt} \right]
\]

where \( \frac{\partial T}{\partial y} \bigg|_{y=h} = 0 \), \( \int_{y=0}^{h} \frac{g(t)}{k} \, dy = \frac{g(t)h}{k} \), \( \alpha = \frac{k}{\rho C_p} \), \( \frac{dh}{dt} = 0 \)

After the substitutions, Equation (40) becomes:

\[
\frac{\partial T}{\partial y} \bigg|_{y=0} + \frac{g(t)h}{K} = \frac{1}{\alpha} \left[ \frac{\partial}{\partial t} \int T \, dy \right]
\]

Where K is the thermal conductivity in W/m·K, \( \alpha \) is the thermal diffusivity in m²/s, and g(t) is defined as follows:
(42) \[ g(t) = H_r \rho_r \frac{d\beta}{dt} = H_r \rho_r (K_t + K_p \beta^n) (1 - \beta)^n \]

where \( H_r \) is the heat of reaction of the resin in J/kg, \( \rho_r \) is the density of the resin in kg/m\(^3\), \( d\beta/dt \) is the isothermal rate of cure in 1/s, which has been determined in Chapter 4.

From the applications of the boundary conditions of Eqs. (36) and (37) to Eq. (39), the coefficients were defined in the following manners:

(43) \[ A = T_{foam}(t) \]

(44) \[ B = -2Ch \]

Therefore, \( T \) inside the integral of the Eq. (41) can be defined using the polynomial representation of Eq. (39) as follows:

(45) \[ T = T_{foam}(t) - 2Chy + Cy^2 \]

Substituting above equation into Eq. (41), evaluating the integral, and simplifying the expression results in:

(46) \[ \frac{2}{3} h^2 \frac{\partial C}{\partial t} + 2C\alpha = \frac{\partial T_{foam}}{\partial t} - \frac{H_r}{C_p} \frac{d\beta}{dt} \]

This is an ordinary differential equation in terms of the coefficient C, knowing that the right-hand side can be defined by the constants and the cure kinetics models of the polyurethane foam and the resin, as discussed in Chapters 3 and 4. An initial condition associated with Eq. (46) may be determined by evaluating Eq. (45) at \( t=0 \). From an initial condition as defined by Eq. (38):
\[ T(y,0) = T_{\text{ambient}} = T_{\text{foam}}(0) - 2C(0)hy + C(0)y^3 \]

However, it is known from the initial condition that \( T_{\text{foam}}(t) = T_{\text{ambient}} \). Therefore, the associated initial condition for the ordinary differential equation of Eq.(46) is:

\[ C(0) = 0 \]

Once Eq.(46) is solved and the value of the coefficient \( C \) is obtained, the value of the coefficient \( B \) may be determined from Eq.(44). Then the theoretical temperature profile of Eq.(39) can be solved by substituting those coefficients. However, the material properties \( \alpha, H_p \), and \( C_p \) for the resin, as well as the thickness \( h \), were not available for this work. Therefore, it was not possible to validate the model derived from the heat-balance integral method. Since this analysis is still at the preliminary stage, it was determined that the exact values of the material properties and the geometries should be used in order to minimize the sources of the error. Therefore, the work done in this chapter should be regarded as one of the possibilities in analyzing the interaction problem involving the chemical reactions of the polyurethane foam and the resin.
CHAPTER 6

Conclusion

6.1 Accomplishments

In this work, the chemical kinetics and the heat transfer effect of the polyurethane foam and the fiberglass-reinforced general purpose resin were studied. Several experimental temperature profiles during the reactions of the foam, the resin, and the two combined, were extensively used to analyze the theoretical cure models of each material as well as the interactions between the two.

An adiabatic method, widely used by many investigators, was applied to the sole temperature profile of the polyurethane foam as a first approach. Despite of several assumptions, the theoretical model known as an autocatalytic type, with kinetic parameters determined by the nonlinear least squares curve fit, has given a desirable fit to the experimental data. Other model, known as the n-th order type, also had a desirable output with comparable result to that obtained by the simplified parameter determination method, indicating that the kinetic parameters in the n-th order model are acceptable values. However, due to this model having slightly higher least-squares error between the theoretical and the experimental temperature profiles, the autocatalytic model was chosen to be the theoretical model representing the polyurethane foam cure.

A heat loss of the polyurethane foam, which takes place after the reaction reaches the completion, was also analyzed using the energy balance equation and the experimental data. However, because of having an average modified heat transfer coefficient and the inaccurate data representation by the best-fitting polynomial, the result was not a perfect fit. Errors are apparent between the theoretical model and the experimental data in several locations on the temperature profile.
The curing process of the fiberglass-reinforced resin was studied using the relationships of the isothermal degree and the rate of cure of the resin. A definition of the heat was applied to the temperature profiles, in order to compensate for the DSC measurements of the degree and the rate of cure. A nonlinear least-squares curve fit was used in order to obtain the kinetic constants in the cure model. The result was very consistent in a way, that all of the initial values taken from the literature have converged to one set of kinetic parameters. It was found that several more experiments of similar procedure should be performed in order to study the resin in depth, so that the theoretical model may be applied to the resin cure at different curing temperatures. This procedure enables the analysis of reaction temperature behaviors of this particular resin at a given cure temperature.

The interaction between the polyurethane foam and the resin was also analyzed. An appropriate approach based on the law of conservation of energy together with the cure kinetics expressions for the foam and the resin was discussed. However, in order to obtain a simplified analytical solution, a heat-balance integral method was considered. Two boundary conditions, one initial condition, and the heat balance integral were applied to the assumed temperature profile of the second-order polynomial, or the parabola. This has given the coefficients in the temperature profile to be expressed by the defined values, such as the cure kinetics models of the polyurethane foam and the resin, and the geometry and the properties of the material. However, because of the several missing constants, the ordinary differential equation in terms of one of the coefficients was not solved. Therefore, this model derived from the heat-balance integral method was not tested for its validity. But rather, the result obtained in this work should be referenced to as one of the possibilities in analyzing the interaction problem involving the chemical reactions of the polyurethane foam and the resin.

6.2 Recommendations for the Future Work

In conclusion, it will be very interesting to solve the ordinary differential equation obtained by the heat-balance integral method in Chapter 5. This process should verify
whether this proposed model would be an appropriate start in analyzing the interaction problem or not. Also the cases, when \( \delta(t) \neq h \), which are more likely to be encountered in real life, should be considered. It is recommended that the several missing information be prepared accordingly, in order to minimize the sources of error in the analysis. These include the material geometries and the properties, and the data generated by the differential scanning calorimeter, which is necessary in order to determine the point of a reaction completion for the resin during the interaction.

At the same time, an approach involving the coupled energy equations for both the polyurethane foam and the resin is another interesting method to be applied to the interaction problem.
REFERENCES


