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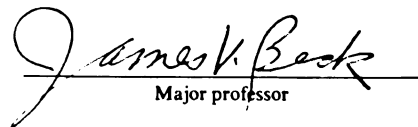This is to certify that the

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ESTIMATION OF THE THERMAL AND KINETIC PROPERTIES
ASSOCIATED WITH CARBON/EPOXY COMPOSITE MATERIALS
DURING AND AFTER CURING

presented by

Elaine Patricia Scott

has been accepted towards fulfillment
of the requirements for

_____Ph. D._____ degree in ___Mechanical___ Engineering

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Major professor

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ESTIMATION OF THE THERMAL AND KINETIC PROPERTIES ASSOCIATED WITH CARBON/EPOXY COMPOSITE MATERIALS DURING AND AFTER CURING

By

Elaine Patricia Scott

A DISSERTATION

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Mechanical Engineering

1989

ABSTRACT

ESTIMATION OF THE THERMAL AND KINETIC PROPERTIES
ASSOCIATED WITH CARBON/EPOXY COMPOSITE MATERIALS
DURING AND AFTER CURING

By

Elaine Patricia Scott

The use of high performance composite materials in a variety of applications has grown rapidly in recent years. A thorough understanding of these materials with regards to thermal characteristics properties is essential in developing new processing methods and product applications. The focus of this research is on the estimation of the thermal properties (specifically thermal conductivity and the product of density and specific heat) of cured carbon fiber/amine-epoxy matrix composites, and on the estimation of both thermal and kinetic properties of these materials during curing. The kinetic properties include the activation energy constants.

The thermal properties of the cured composites were first estimated using an estimation procedure based on the minimization of a least squares function which incorporates both calculated and measured temperatures. Differential scanning calorimetry (DSC) was used in the next phase of this study for the estimation of the kinetic parameters associated with the curing of an EPON 828 amine-epoxy system, using several different kinetic models.

The final phase of this study related to the estimation of thermal properties during the curing process. The simultaneous estimation of thermal conductivity and the product of density and specific heat during the curing process has not previously been attempted. A least squares function incorporating both calculated and measured

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temperatures was again used, and the heat generation resulting from the kinetic reactions during curing was accounted for in the analysis, using the results of the DSC analysis. This procedure was evaluated using simulated temperature data. In addition, an experiment was designed and evaluated for use in obtaining temperature data during the curing process with this estimation scheme.

The thermal conductivity perpendicular to the fiber axis and the density-specific heat were determined for the cured AS4-EPON 828 composite materials as functions of temperature for two different fiber orientations. The kinetic parameters obtained for EPON 828 epoxy were in good agreement with previously published kinetic data for similar epoxy systems during the first half of the curing cycle, and a new reaction rate model was presented for the second half of the curing process. Finally, the procedure for the estimation of thermal properties during curing was verified using simulated temperature data, and improvements were proposed for the techniques and equipment used in obtaining experimental temperatures.

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    the Fiber Ax

    [0°, ±30°, ±

    Experiments

Table C.8 Estimat

    the Fiber Axi

    [0°, ±30°, ±6

    Experiments

LIST OF FIGURES

ae_1	Primary
ae_2	Second
ae_3	Tertiary
$A_1 A_2 A_3$	Pre-exp
b	Estima
	density
B	Amine
B^{avg}	Averag
$c_1 . c_2 . c_3$	rate co
$c'_1 . c'_2$	rate co
c_p	Specif
C	Epoxi
C_1	Initial
C_{ij}	Comp
D	Diffus
$D_1 . D_2$	Regres
	tempe
e	Epoxi
$E_1 E_2 . E_3$	Activa
H	Heat o
$\dot{H}$	Heat g
$\dot{H}$	Gain f
$\bar{H}_o$	Total
	Reside

LIST OF SYMBOLS

ae_1 Primary amine

ae_2 Secondary amine

ae_3 Tertiary amine

A_1 ,A_2 ,A_3 Pre-exponential factors used in kinetic models

b Estimated parameter vector; contains thermal conductivity (W/m°C) and density-specific heat $(J/m^3 \ °C)$ values

B Amine to epoxide equivalency ratio

B^{avg} Average of binary temperature data

c_1 ,c_2 ,c_3 rate constants (s-1) in epoxide reactions

c_1' ,c_2' rate constants (s-1) in resident epoxide reactions

c_p Specific heat (J/kg°C)

C Epoxide consumed in kinetic reactions during curing (moles)

C_0 Initial epoxide in kinetic reactions during curing (moles)

C_{ij} Components of the optimal experimental design criterion

D Diffusion constant

D_0 ,D_1 Regression parameters for the diffusion constant, D, as a linear function of temperature

e Epoxide

E_1 ,E_2 ,E_3 Activation Energy Constants (kJ/mole)

H Heat of reaction (J)

g Heat generation (constant) $(J/m^3 \ )$

g_1 Gain for ith thermocouple (°C)

H_t Total heat of reaction (J)

HX_0 Resident hydroxyl (impurities)

HX_a	Hydr
k	Ther
k_{eff}	Effec
k_f	Ther
k_m	Ther
k ,k ,k	Regres
	peratu
L	Thickn
m	Expone
m ,m_i	Regress
	ture
n	Expone
n_t	Numbe
n ,n_i	Regress
	ture
P	Marchi
q	Heat flu
R	Gas con
S	Least s
t	Time (s
t^a	Time at
t	Total h
t	Time a
	(sec)
T	Temper
T	Temper
T_{ar}	Maximu
	design
T	Initial t
	Calcula

HX_a	Hydroxide group resulting from amine-epoxide addition reaction
k	Thermal conductivity (W/m°C)
k_{eff}	Effective thermal conductivity (W/m°C)
k_f	Thermal conductivity of fibers (W/m°C)
k_m	Thermal conductivity of matrix (W/m°C)
k_1, k_2, k_3	Regression parameters for thermal conductivity as a linear function of temperature and degree of cure
L	Thickness (m)
m	Exponential constants in kinetic models (dimensionless)
m_0, m_1	Regression parameters for the exponent, m, as a linear function of temperature
n	Exponential constants in kinetic models (dimensionless)
n_t	Number of experimental time steps
n_0, n_1	Regression parameters for the exponent, n, as a linear function of temperature
P	Marching direction in steepest descent method
q	Heat flux (W/m^2)
R	Gas constants (mole°K/kJ)
S	Least squares function
t	Time (sec)
t^n	Time at nth time step (sec)
t_0	Total heat of reaction (sec)
t_1	Time at the end of the heat flux in optimal experimental design analysis (sec)
T	Temperature (°C)
T_L	Temperature at boundary where $x = L$ (°C)
T_{max}	Maximum temperature up to time nth time step in optimal experimental design criterion analysis (°C)
T_0	Initial temperature (°C)
$\mathbf{T}$	Calculated temperatures (vector) (°C)

r	Measured
rᵃ	Adjusted
V_f	Fiber vol
w	Weightin
x	Position
x	Sensitivit
Y	Measured
z	'Zero' adj
a	Degree of
b	Degree of
a_p	Degree of
g	Weighting
l	Eigenvalu
q	Paramete
	specific
q̂	Paramet
	mal con
r	Density
c_p	Density
c_p, c_{p^2}	Regress
c_{p^3}	tion of
D	Optima
Y	Matrix

V	Measured thermocouple voltage (volts)
V^a	Adjusted thermocouple voltage (volts)
V_f	Fiber volume fraction (dimensionless)
W	Weighting matrix for least squares function
x	Position along the x-axis (m)
X	Sensitivity coefficient matrix
Y	Measured temperatures (vector) (°C)
z	'Zero' adjustment for thermocouples (°C)
α	Degree of cure (dimensionless)
α_D	Degree of cure where diffusion becomes significant
α_p	Degree of cure at maximum degree of cure rate (dimensionless)
$\underline{\alpha}$	Weighting factor in steepest descent method
β	Eigenvalues
$\underline{\beta}$	Parameter vector; contains thermal conductivity (W/m°C) and density-specific heat (J/m³ °C) values
$\hat{\underline{\beta}}$	Parameter vector from minimization of least squares function; contains thermal conductivity (W/m°C) and density-specific heat (J/m³ °C) values
ρ	Density (kg/m³)
ρc_p	Density-specific heat product (J/m³ °C)
ρc_{p^1} , ρc_{p^2} , ρc_{p^3}	Regression parameters for thermal conductivity as a linear function of temperature and degree of cure
Δ	Optimal experimental design criterion
$\underline{\nabla}$	Matrix derivative operator

<u>Superscripts</u>

+	dimensionless

<u>Subscripts</u>

T	top
B	bottom

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Chapter 1

Introduction

In general, a composite is simply the combination of two or more materials to obtain a new material with some improved or new characteristics, particularly with regards to strength and weight. The use of composite materials in construction and vehicle applications has been in effect since the early Egyptian days when bricks and boats were fabricated from mud fortified with reeds and chopped straw. However, the widespread use of modern day composites, which utilize new high-performance materials, has only come into being during the last 20 years. These high-performance materials are commonly associated with the aeronautics and aerospace industries, especially with regards to the military, where composites are particularly attractive due to their generally low-weight/high-strength characteristics. One of the most notable use of composites was in the design of the all-composite Voyager aircraft, which proved the strength and durability of the materials in its non-stop flight around the world.

However, the use of high-performance composites is by no means limited to the aero-related industries. The automotive industry has used composites in body and suspension components, and the boating industry has incorporated composites in hull and rudder designs. The U.S. Navy has a particular interest in composites in ship and submarine designs. Another important industry is the sporting goods industry, which has produced a multitude of composite golf clubs, tennis rackets, racket ball rackets, rowing oars, bicycles, skis, and poles for pole vaulting designed to give the athlete, or would be athlete, the extra edge to hit harder, go faster, and jump higher.

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Modern day composites are formulated in a variety of ways from many different materials. Due to this variability, they are often classified as fiber, particulate, laminar, flaked or filled (Vinson and Sierakowski, 1987). The fiber-reinforced composites are of particular interest in this study. These composites are typically composed of strength enhancing fibers bound together in a relatively low density matrix material. The fibrous materials include glass, Kevlar, carbon, and boron, and the matrix materials include epoxies, polymides, phenolics and aluminum. The focus of this study is on continuous carbon fiber-epoxy matrix composites. The epoxies used in these composites are classified as thermoset materials since both heat and pressure are required for the epoxy to cure and thus bind to the fibers.

It is the application of heat on composites both during and after curing that has provided the motivation for this study. The thermal responses of cured composites to applied heat loads induce thermal stresses, which can possibly lead to structural failure. Accurate knowledge of the thermal characteristics of the composites are, therefore, very important with regards any design application in a nonisothermal environment. The thermal response of composites is also pertinent with respect to the design of the curing cycle. In the worst case scenario, a lack of understanding of the thermal characteristics of the composite during curing could lead to an unevenly cured product which is structurally unsafe. In the best of worlds, a thorough understanding of these thermal characteristics would lead to the design of an optimal curing cycle which maximizes product quality and minimizes cost.

The thermal responses of interest in this study are the result of applied heat fluxes which lead to conductive heat transfer within the composite. These thermal responses are characterized by the intrinsic thermal properties of the particular composite material, namely the thermal conductivity and the density-specific heat product. In addition, during curing, the epoxy matrix composites of interest undergo exothermic reactions, in which the rate of heat generation is characterized by the kinetic properties of the composite. It is the determination of these thermal and kinetic properties which is the focal point of this study. The particular composite used in this study consists of AS4 fibers (Hercules Aerospace Corp.) and with an EPON 828 epoxy matrix (Shell

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Chemical Comp.). This is a moderate temperature (<150°C) high-performance composite with a high strength versus weight ratio. The emphasis in this study was not only on the determination of specific properties values, but also on the development of both the analytical and experimental procedures for the estimation of these properties, which are not necessarily limited in application to the specific composite investigated here.

The overall objectives of this study can be divided into three major areas: the estimation of thermal properties in cured composites; the estimation of kinetic properties during curing; and, the estimation of thermal properties during curing. In the estimation of thermal properties of cured composites, a minimization procedure involving a least squares function is employed which utilizes experimental temperature measurements within the composite. This approach is unique in that the experiments are transient and both the thermal conductivity and density-specific heat properties are estimated simultaneously. Previous studies (Lee and Taylor, 1975; Ishikawa, 1980) have typically measured these two properties in composites in independent experiments. This approach has been used, however, for homogeneous materials (Beck and Al-Araji, 1974; Courville and Beck, 1988; Farnia, 1976), and the emphasis in this particular instance is on developing an experimental design and on obtaining specific property values as functions of temperature. The specific objectives are to estimate the thermal conductivity perpendicular to the fiber axis direction and the density-specific heat product of cured AS4/EPON 828 composite materials as functions of temperature and fiber orientation.

The second area of interest is the estimation of kinetic properties during curing. This is shown to be fundamentally linked to the third overall objective relating to the estimation of thermal properties during curing. The kinetic properties are those parameters which characterize the chemical reactions during curing, and they include rate constants and activation energy constants. These properties are estimated using established procedures using differential scanning calorimetry (DSC). Unlike previous studies (Sourour and Kamal, 1976) which have only focused on the first half of the cure cycle, the effort of this study was to estimate the kinetic properties which characterize

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the exothermic reactions throughout the entire cure cycle. The kinetic properties which characterize these reactions typically involve the determination of rate constants which are assumed to follow an Arrhenius relationship (Barton, 1985) with temperature. In this case, efforts were directed towards obtaining specific properties values which could be used in the estimation of thermal properties during curing. The specific objectives in this area were to estimate the kinetic properties associated with the curing of EPON 828 epoxy from DSC data using the various kinetic models found in the literature for similar epoxy systems, and to select the most appropriate model(s) for this particular epoxy system.

Previous efforts for the estimation of thermal properties during curing required the interruption of the curing process and/or separate experiments for each property measurement (Mojovic and Mei, 1987). The focus of this investigation is new and unique because the procedures permit the thermal properties, namely thermal conductivity and density-specific heat, to be measured simultaneously throughout the curing process as functions of both temperature and completeness or degree of cure. The estimation problem is difficult in both the analytical and experimental aspects.

The proposed procedure involves the minimization techniques utilized in this study for the estimation of the thermal properties of cured composites; however, this analysis is complicated by the exothermic chemical reactions occurring during curing. This estimation procedure also required transient temperatures measurements, which necessitated the development of new experimental designs applicable during the curing process. Due to the complexity of this problem in both analytical and experimental aspects, the focus of these efforts were on the development of the estimation procedures, rather on obtaining specific property values. Therefore, the specific objectives in this case are first to develop and verify the analytical procedures for the estimation of thermal conductivity and density-specific heat during curing. This would incorporate the parameter estimation techniques utilized in this study for the estimation of thermal properties of cured composites and the results of the kinetic analysis of the EPON 828 epoxy system. The second objective involves the development and testing of an appropriate experimental design for use in recording transient temperature measurements

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Chapter 2

Literature Review

A review of the literature for the estimation of thermal and kinetic properties in composite materials is given in this chapter. In the first section, the emphasis is on the estimation of thermal properties in cured composites. There have been many studies in this area with regards to both theoretical and experimental methods. The next section is devoted to the techniques used in estimating kinetic properties of epoxy-based composite systems during curing. These methods utilize differential scanning calorimetry to estimate rate constants which characterize the curing of the composites. The techniques which have been used to estimate thermal properties during the curing process are presented in the third section. This is followed by a final section on minimization methods which have been used to estimate thermal properties in homogeneous materials. These methods provide a means of coupling experimental measurements with analytical solutions, and they allow for the simultaneous determination of both thermal conductivity and the product of density and specific heat.

2.1 Estimation of Thermal Properties of Composite Materials

The methods used for the estimation of thermal properties in cured composite materials have included both experimental and analytical techniques. A synopsis of the techniques used to estimate thermal properties in composite materials and other related anisotropic materials is first presented in Section 2.1.1. This is followed by a

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review of previous research devoted to the estimation of thermal properties of carbon fiber-reinforced composites, in particular.

2.1.1 Estimation of Thermal Properties of Composite and Other Anisotropic Materials

The problem of estimating thermal properties, such as thermal conductivity, in anisotropic composites is interesting and challenging in that not only is the directional aspect of importance, but also because composites, by definition, are composed of at least two different types of materials (i.e., the fiber and matrix materials), with differing thermal properties. The existing literature on this subject indicates that research has been concentrated in two different areas for the solution of this problem.

The first area is focused on the determination of the effective or overall thermal properties from a mathematical analysis of the components of the composite. The estimation of thermal conductivity, in particular, has been the main focus of the studies in this area. Most of these methods are based on the assumption that the thermal conductivities of the individual composite elements, namely the matrix and the fiber, are known, along with the void fraction of the fibers. These models are based on the original theories by Maxwell and Rayleigh (Hasselman and Johnson, 1987). Several such models for the effective thermal conductivity of composites were proposed by Hasselman and Johnson (1987). These models also required knowledge of the fiber diameter and the interfacial thermal barrier resistance between the fiber and the matrix. Ziebland (1977) presented a simpler approach in which the effective thermal conductivity was calculated using a unit-cube model with rectangular coordinates. The model for the heat flux perpendicular to the fiber length (fiber and matrix in series) is expressed mathematically as

$$k_{eff} = \frac{k_m k_f}{V_f k_m + (1-V_f)k_f}$$

where k_{eff} is the effective thermal conductivity of the composite, k_m and k_f are the thermal conductivities of the matrix and the fiber, respectively, and V_f is the fiber volume

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fraction. Ziebland also included models for cross-plied and fabric laminates. James et al. (1987) also used the unit-cube approach, but with a cylindrical model for the fiber. Combining this approach with a finite difference model for heat flow within composites, a generalized expression was obtained for the effective thermal conductivities in off-axis directions, given the effective thermal conductivity parallel and perpendicular to the fiber axis. Similarly, Mottram and Taylor (1987b) developed expressions for effective thermal conductivity parallel and perpendicular to the fiber axis, which included both one and two-directional composite laminates. Han and Cosner (1981) analyzed the effective thermal conductivity of composites with different void fractions, using a finite element analysis of a unit composite cell, with heat flow perpendicular to the fibers. A numerical method was presented by Dul'nev et al. (1977) which combined Rayleigh's method with the method of grids to estimate the effective thermal conductivity of a composite. In this procedure, each block defined by a grid was analyzed as a two component system using Rayleigh's approach.

The other focus of attention for the determination of the thermal properties has been on experimental methods. In the estimation of thermal conductivity, most of these experimental methods are conducted at steady state conditions. Most of these methods involve one or two thin samples which are placed in between heated or cooled plates. Ziebland (1977) describes these methods as absolute, where thermal conductivity is determined solely from and energy balance of the steady state conditions, or relative, where thermal conductivity is determined by reference to a substance of known thermal conductivity. Three of the absolute methods mentioned by Ziebland are the flat plate apparatus with a heater guard, which uses one flat test specimen, the coaxial cylinder cell with heater guard, which uses a cylindrical test specimen, and a two-plate apparatus, which uses two test specimens and is generally preferred. Harris et al. (1982) used the later method in estimating the thermal conductivity of Kevlar fiber-reinforced composites as a function of temperature and fiber direction. The relative methods involve apparatus similar to the two-plate apparatus, but they are more complex in their construction. Quasi-steady state experiments, using similar apparatus, were also discussed by Ziebland for materials with low thermal conductivity.

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Another technique for the experimental determination of thermal diffusivity, heat capacity, and thermal conductivity is the laser-flash method presented by Parker et al. (1961). In this method, a laser pulse is directed on a sample a few millimeters thick which is coated with carbon to prevent direct transmission of the beam, and the temperature response of the specimen at the rear surface is monitored by optical means. The thermal diffusivity is then determined from the time required for the back surface to reach one half of the maximum temperature rise, and the heat capacity is determined from the maximum temperature rise of the specimen. The thermal conductivity can be determined from the thermal diffusivity, the heat capacity, and the density. This method was used by Brennan et al. (1982) to determine the thermal conductivity and thermal diffusivity of thin amorphous silicon carbide fibers from composite and neat matrix samples as functions of temperature, and by Mottram and Taylor (1987a) to determine the thermal diffusivity of silica-phenolic composites.

Other methods have also been considered in the determination of thermal properties. Beck and Al-Araji (1974) presented a method of estimating thermal conductivity and density-specific heat independently from a single transient experiment. Schimmel, Jr. et al. (1977) presented a solution for the determination of the effective thermal conductivity of a multi-layer laminate based on an analytical solution for a two-layer composite transient system with known thermal properties of the components. A method of estimating thermal conductivity in unidirectional materials which is analogous to the problem of longitudinal shear loading of a unidirectional composite, where the thermal conductivity is analogous to the average shear moduli, was proposed by Springer and Tsai (1967). This method was compared to a thermal model in which the filament and matrix were assumed to be arranged in series.

2.1.2 Estimation of Thermal Properties of Cured Carbon Fiber Composites

Most of the previous research on the estimation of thermal properties, such as thermal conductivity and thermal diffusivity, of carbon fiber-reinforced composite materials has been for cured composites. The methods used in the determination of

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these properties included some of the techniques described in Section 2.1.1., and they included both experimental and analytical aspects.

The laser-flash method (Parker et al. 1961) was used by Lee and Taylor (1975) along with an absolute method, which required cylindrical samples, to determine the thermal diffusivity and the effective thermal conductivity of carbon fiber-reinforced (PX 505) and graphite fiber-reinforced (Morganite II and Thornal 50 S) composites. The thermal diffusivities of the graphite fibers were determined from the effective thermal conductivities estimated using the absolute method. Taylor and Kelsic (1986) investigated the effects of fiber fraction, fiber/matrix thermal conductivity ratio, fiber orientation, and specimen length on thermal diffusivity of unidirectional fiber-reinforced composites using the laser-flash technique. They found that the conductivity ratio, followed by the fiber volume fraction were the major factors affecting the thermal behavior of the composite. Mottram and Taylor (1987a) also used the laser-flash method to determine thermal diffusivity of woven and unwoven carbon fiber-phenolic resin composites as a function of temperature. This work was continued (Mottram and Taylor (1987b), and the thermal conductivity of the carbon-phenolic composite was determined in different fiber directions using the Maxwell-Rayleigh approach.

Ishikawa (1980) analytically determined the thermal conductivity of carbon/epoxy composite systems under steady-state conditions using a Fourier series analysis based on the solution of the longitudinal shear problem. This is the same approach used by Springer and Tsai (1967). This solution was two dimensional, and it required knowledge of the thermal conductivity of the matrix and the fiber volume fraction. The analytical results were compared with experimental results using a technique called the infrared radiation method.

2.2 Estimation of Kinetics Parameters in Epoxy-Based Systems

The kinetic parameters of importance in this section include the rate constants and activation energy constants which characterize the curing of amine-epoxy based composite systems. A discussion of the cure kinetics of amine-epoxy systems is first

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presented, followed by review of differential scanning calorimetry. A summary of previous studies in the estimation of kinetic parameters in amine-epoxy systems is then given; these studies all utilize experimental results obtained using differential scanning calorimetry. Finally, a brief discussion is included on the use of neat vs. reinforced composite systems with regards to the estimation of kinetic parameters.

2.2.1 Kinetics of Amine-Epoxy Systems

The epoxy system of interest in this investigation is an amine-epoxy system in which the initial reaction is accelerated due to autocatalyzation, while in the latter stages, the reaction is diffusion controlled. Due to the complexity of the system, researchers have used relatively simple models over limited ranges of conversion to describe the kinetics of the reactions.

Most of the reaction models for the initial phase of the amine-epoxy cure are based on the mechanisms proposed by Schechter et al. (1956) and Smith (1961). The rate determining step of the reaction scheme is assumed to be the reaction of amine, epoxide and hydroxyl (or other proton-donor species, HX) (Barton, 1985). This scheme is a two tiered process, which involves reactions of the hydroxyls formed in the amine-epoxide reactions, HX_a, and the resident hydroxyls in the system (impurities or additives), HX_o:

$$a_1 + e + HX_a \xrightarrow{c_1} a_2 + HX_a$$

$$a_1 + e + HX_o \xrightarrow{c_1'} a_2 + HX_o$$

$$a_2 + e + HX_a \xrightarrow{c_2} a_3 + HX_a$$

$$a_2 + e + HX_o \xrightarrow{c_2'} a_3 + HX_o$$
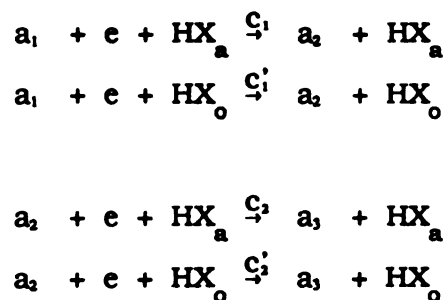
In these reactions, a_1, a_2, and a_3 are primary, secondary, and tertiary amines, e is the epoxide, and the c_i and c_i' values (i = 1, 2) are the reaction rates. From this scheme, the following overall kinetic equation was derived (Barton, 1985):

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$$\frac{dC}{dt} = (c_i' \, C_o + c_i \, C)(e_o - C)(a_i + a_i)$$ (2.1)

where C is the epoxide consumed at a given time, t; C_o and e_o are the initial concentrations of HX_o and the epoxide, respectively; and, a_i and a_i are the concentrations of the primary and secondary amines.

2.2.2 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) has been defined by the Nomenclature Committee of the International Confederation for Thermal Analysis (ICTA) as a technique in which the difference in energy inputs into a substance and reference material are subjected to a controlled temperature program (Barton, 1985). The technique of DSC has proven to be a useful method for the investigation of exothermic reactions, such as those occurring during the curing of epoxy resins (Fava, 1968; Rabek, 1980). The underlying assumption in DSC kinetics is that the difference in heat flow between the reacting substance and the reference material is proportional to the reaction rate (dC/dt in eq. 2.1).

There are two types of DSC instruments. The first operates under a power compensation mode which utilizes separate sample and reference holders with individual heaters and platinum thermometers. The second type operates in a heat flux mode; the sample and reference are in separate containers connected by a controlled thermal resistance with external thermocouples. The DuPont Instruments 910 Differential Scanning Calorimeter cell, used in this study, operates in the heat flux mode. This cell consists of a sample chamber in which the empty reference and sample pans rest on an enclosed platform instrumented with thermocouples. In using both the power compensation and the heat flux DSC instruments, it is assumed that the temperature gradients within the sample are very small. This requires the use of small samples (on the order of milligrams) and the assurance of good thermal contact between the sample and the sample pan, and the same degree of thermal contact between the sample pan and the platform, and the reference pan and the platform.

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Two experimental methods involving the use of DSC are commonly used in the kinetic modeling of exothermic systems. In the first instance, isothermal experiments are conducted at different temperatures, and the rate of heat flow is recorded with time. By assuming an appropriate kinetic model, rate constants can be determined for each temperature studied, and then the relationship between these rate constants and temperature can be determined. The second method involves dynamic experiments in which a sample is heated at a linear rate throughout the curing process. This is sometimes referred to as the Borchardt and Daniels method (Borchardt and Daniels, 1957). In this case, both the time and temperature dependence of the conversion rate (which is proportional to the reaction rate) may be found simultaneously. Use of this method has been limited to very simple kinetic models in which only one rate constant is found (i.e., nth order kinetics).

2.2.3 Cure Kinetics using DSC

Several researchers have used a generalized form of eq. (2.1) to identify rate constants of a bisphenol-A-diglycidylether (BADGE) and meta-phenylenediamine (mPDA) epoxy system, which is similar to the epoxy investigated here. The kinetic model contains two rate constants, consistent with the mechanisms presented by Barton (1985). The first rate constant, c_1, represents nth order kinetics, while the autocatalytic nature of the reaction is evident by the second rate constant, c_2. Therefore, if no impurities are present, c_1 is equal to zero, and the reaction is completely autocatalyzed. The generalized kinetic equation is

$$\frac{d\alpha}{dt} = (c_1 + c_2 \alpha^m)(1 - \alpha)^n \qquad (2.2)$$

where, α is the fractional conversion, and m and n are constants. Ryan and Dutta (1979) used this model to determine the rate constants c_1 and c_2 from maximum reaction rate data from isothermal DSC experiments, assuming a second order reaction (m + n = 2). An Arrhenius relationship was assumed between the rate constants and temperature:

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$$c_i = A_i \exp(-E_i / RT) \qquad\qquad i = 1, 2 \qquad\qquad (2.3)$$

This relationship was shown to follow conversion rates up to 90%, with no evidence of a diffusion controlled reaction.

Equation (2.2) was also used by several researchers to describe curing in other similar epoxy systems. Mijović et al. (1984) used this model to determine rate constants in an tetraglycidyl-4,4'diminodiphenylmethane epoxy system, and Moroni et al. (1986) used this model in studying BADGE and 1,4 butanedioldiglycidylether resin mixtures. In studying curing kinetics in BADGE/ethylenediamine epoxies, Chern and Poehlein (1987) used this model and found that diffusion controlled the reaction rates for values of $\alpha > 58\%$. Hagnauer et al. (1983) also used this model to investigate the cure kinetics in glass fiber-BADGE epoxy systems.

In an earlier study, Sourour and Kamal (1976) assumed $m = n = 1$ and used

$$\frac{d\alpha}{dt} = (c_1 + c_2 \alpha)(1 - \alpha)(B - \alpha) \qquad\qquad (2.4)$$

where B is the amine to epoxide equivalency ratio. The rate constants were determined using isothermal DSC experiments, and the activation energy constants were found assuming an Arrhenius relationship. This relationship followed for values of α up to 40 or 50%; at that time, the reaction rate decreased, indicating a diffusion controlled reaction for conversion rates greater than 50%. Likewise, Lee et al. (1982) used this model in studying Hercules 3501-6 resin and found that the reaction was diffusion controlled for $\alpha > 30\%$.

Prime (1973) implemented a simpler equation to describe curing in the BADGE/mPDA system incorporating both isothermal DSC experiments and dynamic DSC experiments which utilized the Borchardt and Daniels (1957) method. In this model, and nth order reaction is assumed with no autocatalyzation (c_2 is zero):

$$\frac{d\alpha}{dt} = c_1 (1 - \alpha)^n \qquad\qquad (2.5)$$

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Deviations from this model were found for higher conversion rates, where the reaction was assumed to be diffusion controlled. Acitelli, et al. (1971) found similar results in an investigation of the cure of BADGE/mPDA epoxy. Pappalardo (1977) also used this model to investigate glass reinforced-BADGE epoxy prepregs.

Very few models have been developed which incorporate diffusion in the kinetic analysis. Lee et al. (1982) presented the following equation for extent of cure greater than 50% in their study of Hercules 3501-6 resin:

$$\frac{d\alpha}{dt} = c_3 (1 - \alpha) \qquad (2.6)$$

where, c_3 was assumed to follow an Arrhenius relationship (eq. 2.3). Hawley et al. (1988) presented another model for conversion rates greater than 50%, which included an exponential term indicative of the diffusion phenomenon. This model is

$$\frac{d\alpha}{dt} = c_3 (1 - \alpha)e^{-D\alpha} \qquad (2.7)$$

In this equation, D is a diffusion coefficient, and once again, the rate constant, c_3, was assumed to follow an Arrhenius relationship.

2.2.4 Cure Kinetics of Neat vs. Carbon Fiber Reinforced Epoxy Systems

There have been a few studies on the comparison of the cure kinetics of neat versus reinforced epoxy systems. Mijović and Wang (1989) studied the effects of carbon fibers in a tetra-N-glycidyldiaminodiphenylmethane (TGDDM)/dianimodiphenyl-sulphone (DDS) amine-epoxy system, and found that the presence of carbon fibers had only a very small initial effect on the kinetics of cure. In a related study, Mijović (1986) compared the cure kinetics of neat versus glass reinforced TGDDM/DDS epoxy. It was found that in the reinforced system, the reaction rate constants were slightly lower, and the time required to reach the maximum reaction rate was slightly longer. These minor differences were assumed to be the result of restricted mobility due to the reinforcement.

2.3 Estimation

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2.3 Estimation of Thermal Properties in Carbon/Epoxy Composite Systems during Curing

The estimation of thermal properties in composite materials during curing is complex due to the exothermic reactions which occur as the epoxy matrix cures. In order to estimate thermal properties during curing, the curing process itself must be first understood with regards to the heat transfer process. The mathematical models used simulate heat transfer during the curing process are first reviewed. This is followed by a review of the previous work in the estimation of thermal properties during curing, which to date is quite limited.

2.3.1 Mathematical Models to Simulate Heat Transfer in Carbon/Epoxy Composite Materials during Curing

Several researchers have developed mathematical models to simulate heat transfer in cured composite materials (e.g. Golovchan and Artemenko, 1987), but few have developed models to describe heat transfer in composites during the curing process. Loos and Springer (1983) developed models to describe the curing process of composites constructed from continuous fiber-reinforced, thermosetting resin matrix prepreg materials. A computer program was developed which provides the temperature distribution, degree of cure of the resin, the resin viscosity inside the composite, the void sizes, and the residual stress distribution given a specific process for a flat plate composite. In the mathematical model for temperature, a term was added for the heat generated by chemical reactions which was proportional to the rate of degree of cure.

More commonly, researchers have focused on modelling another process which is mathematically related to the curing process, namely decomposition. Both processes have added terms in the energy equation which are proportional to the chemical reaction rate for the process (curing or decomposition). Tant et al. (1985) developed and tested a mathematical model including a decomposition term for the thermochemical expansion of polymer composites during pyrolysis. Henderson et al. (1985) developed a

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model for the thermal response of a polymer composite material undergoing decomposition assuming one dimensional heat transfer and nth order kinetics for the rate of decomposition. Using a similar approach, Boyer and Thomas (1985) and Henderson and Wiecek (1987) investigated charring in composites in terms of thermochemical expansion. Griffis et al. (1981) developed a finite difference model for the thermal response of carbon epoxy composite subject to rapid heating, including the effects of decomposition.

2.3.2 Estimation of Thermal Properties in Composites during Curing

While there have been many studies on the estimation of thermal properties on composites, there have been relatively few studies on the estimation of thermal properties of composite materials during curing.

Mijović and Mei (1987) designed an apparatus for the measurement of thermal conductivity of TGDDM/DDS epoxy carbon fiber composite materials. Using this apparatus, a very thin section (1 mm) composite sample was cured between two parallel plates, allowing for the assumption of a linear temperature distribution across the thickness of the sample. Thermal conductivity was determined as a function of time for different isothermal curing temperatures. In a related study, Mijović and Wang (1988) determined the density and heat capacity (not thermal conductivity) of the same composite during curing. To measure density, samples were cured isothermally at different temperatures for different times and then quenched to prevent further curing. The density of the partially cured samples was then determined using a density gradient column. The heat capacity of the samples during curing was measured using differential scanning calorimetry (DSC). In this procedure, the reference DSC pan contains a substance of known specific heat (DuPont Company Instrument Systems, 1985).

2.4 Minimization Methods used for the Estimation of Thermal Properties

One means of estimating thermal properties involves the minimization of an objective function, such as a least squares function. This is a powerful estimation method,

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but it has been primarily used in the estimation of thermal properties in isotropic materials. There are several different minimization methods; three of the more commonly used methods are the Gauss method, the steepest descent method, and the conjugate gradient method. In each case, the objective function is minimized by selecting the appropriate direction and step size for perturbations in the parameters being estimated. A brief discussion of each of these methods is now presented.

2.4.1 The Gauss Method

The Gauss method is one of the more popular minimization methods. Beck and Arnold (1977) describe this method as being relatively simple and effective for seeking minima which are reasonably well-defined, assuming that the initial estimates are in the general region of the minimum.

In this method, a least squares function is minimized with respect to the unknown parameters (thermal properties) and the resulting expression is set equal to zero. A least squares function given by Beck and Arnold (1977) is

$$S = [\mathbf{Y} - \mathbf{T}(\beta)]^T \mathbf{W} [\mathbf{Y} - \mathbf{T}(\beta)] \qquad (2.8)$$

where the vector $\mathbf{Y}$ contains measured temperatures, β is the parameter vector, the vector $\mathbf{T}$ contained temperatures as a function of β, calculated from the appropriate energy equation for the system being studied, and $\mathbf{W}$ is a weighting matrix. It is assumed in this analysis that the first derivatives of $\mathbf{T}$ are continuous in β and that the higher derivatives are bounded.

When the derivative of the least squares function is set equal to zero, $\beta = \hat{\beta}$, the true minimum of the parameters. This minimization procedure results in terms containing $\mathbf{T}(\hat{\beta})$ and the derivatives of $\mathbf{T}(\beta)$ with respect to the parameters in β, namely, $[\nabla_\beta \mathbf{T}^T(\hat{\beta})]^T$, which is defined as $\mathbf{X}(\hat{\beta})$; In the Gauss method, two approximations are made. First, $\mathbf{X}(\hat{\beta})$ is replaced by $\mathbf{X}(\mathbf{b})$, where the $\mathbf{b}$ vector contains the estimated parameters, and secondly, $\mathbf{T}(\hat{\beta})$ is approximated by the first two terms of a Taylors series about $\mathbf{b}$.

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These approximations result is a linear equation in $\hat{\underline{\beta}}$ which can be solved, iteratively if needed, given an initial estimate of the parameters in **b**.

Beck (1966) used this method in estimating the thermal conductivity and density-specific heat of nickel from transient temperature measurements, and Farnia (1976) used this method in estimating time and temperature dependent thermal properties of 2024-T351 aluminum alloy.

2.4.2 The Steepest Descent Method

The steepest descent method is an alternate approach to the minimization problem (Huag and Arora, 1979). Here, the marching direction is equal to the negative gradient of the objective or least squares function (Lamm, 1989)

$$\mathbf{P}^{(k)} = -\nabla_{\underline{\beta}} S(\underline{\beta}^n) \tag{2.9}$$

and the magnitude of the change in $\underline{\beta}$ in is found from

$$\underline{\beta}^{(k+1)} = \underline{\beta}^{(k)} + \underline{\alpha}^{(k)} \mathbf{P}^{(k)} \tag{2.10}$$

where $\underline{\alpha}^{(k)}$ is a weighting factor such that

$$\underline{\alpha}^{(k)} = ||\mathbf{P}^{(k)}||^2 / ||\partial\mathbf{T}/\partial\underline{\beta}||^2 \tag{2.11}$$

where $||\cdot||$ denotes the norm for a vector, **f**, with p components; it is defined by

$$||\mathbf{f}|| = \left(\sum_{k=1}^{p} f_k^2 \right)^{1/2}$$

The superscript k, eq. (2.9), (2.10), and (2.11) indicates that this is an iterative process.

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2.4.3   The Conjugate Gradient Method

The conjugate gradient method is similar to the steepest descent method, and it has been used to solve both inverse heat conduction problems (Alifanov and Kerov, 1981, and Tu, 1988) and optimal design problems (Huang and Arora, 1979). Alifanov and Kerov (1981) described the method as having good characteristics for solving ill-posed problems, compared with the method of steepest descent. Alifanov and Mikhailov (1979) also used the conjugate gradient method in the solution of the nonlinear inverse thermal conductivity problem.

In this method, the marching directions, $P(\beta)$, for the unknown parameters in β are found using an iterative sequence of the form (Huag and Arora, 1979)

$$P^{(k)} = P^{(k-1)} - \nabla_\beta S(\beta^n) \tag{2.12}$$

The magnitude of the change in $\beta^{(k)}$ is again found from eq. (2.10).

2.4.4   Methods of Determining the Matrix Derivatives

The minimization methods mentioned above involve the determination of the matrix derivative of the least squares function, S, or the temperature, T, with respect to the unknown parameters in β. These derivatives can be found directly, by using finite differences (or elements), or by using the adjoint method (Tu, 1988).

In the direct method, the matrix derivative of S is carried out through matrix differentiation, and the derivatives for T are found by differentiating the appropriate governing equations used to solve for temperature by β, and solving the resulting equation analytically or numerically. If finite differences are used to determine the temperature derivative, a simple forward difference expression can be used. These techniques are discussed in detail by Beck and Arnold (1977).

The adjoint method has been used in design analysis (Tortorelli et al., 1989) and in the solution of the inverse heat conduction problems (Alifanov and Rumyantsev, 1987). This method involves the solution of an adjoining set of equations, in addition to the governing set of equations. These adjoining equations or adjoint equations, as they

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are sometimes called, are solved backwards in time; that is, instead of requiring an initial condition, a terminal condition is required, and the adjoint solution marches backwards in time. Interface conditions, which guarantee continuity at the interfaces where temperature measurements are made, are also included in the adjoint equations.

Chapter 3

Theoretical Considerations

In this chapter, the theoretical development of the analysis used in estimating thermal and kinetic properties of continuous carbon-fiber/epoxy-matrix composite materials is presented. These materials are orthogonal due to the presence of the fibers, resulting in more than one component of thermal conductivity. Due to the complexity of this problem, this study is limited to the estimation of the thermal conductivity perpendicular to the fiber axis. The thermal properties estimated here are effective properties of the composite, and not of the individual fiber and matrix components.

In the first section of this chapter, the techniques used to estimate the thermal properties of cured composite specimens as functions of temperature are discussed. These techniques incorporate the Gauss minimization method (Section 3.4.1). The second section is devoted to theoretical considerations used in the estimation of kinetic properties which characterize the chemical reactions occurring during the curing process. The theoretical methods used in estimating thermal properties as functions of temperature and extent of cure during curing are outlined in the following section. These methods incorporate the techniques discussed in the first section and the results of the analysis presented in the second section. A final section is presented on the development of an optimum design criterion to maximize sensitivity in the estimation of the thermal properties.

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3.1 Estimation of Thermal Properties in Cured Composite Materials

The direct problem of determining the temperature field resulting from conduction heat transfer through a composite specimen is inherent in the procedure used for the estimation of the thermal properties of composite materials. In this section, the direct problem is first defined, and then the solution procedure used for the estimation of the thermal properties is discussed.

3.1. 1 Heat Conduction in Cured Carbon-Fiber Reinforced Composites

One dimensional heat conduction was considered through a cured carbon-fiber/amine-epoxy composite flat plate. For the case where heat conduction due to an imposed heat flux on one surface is perpendicular to the fiber axis and the temperature at the other surface is known, the system can be expressed mathematically as

$$\frac{\partial}{\partial x}\left[k(T)\frac{\partial T}{\partial x}\right] = \rho c_p(T)\frac{\partial T}{\partial t} \qquad 0 < x < L; \qquad t > 0 \qquad (3.1a)$$

with the boundary conditions,

$$-k(T)\frac{\partial T}{\partial x} = q(t) \qquad x = 0; \qquad t > 0 \qquad (3.1b)$$

$$T = T_L(t) \qquad x = L; \qquad t > 0 \qquad (3.1c)$$

and the initial condition,

$$T = T_0(x) \qquad 0 \leq x \leq L; \qquad t = 0 \qquad (3.1d)$$

where x is the direction perpendicular to the fibers through the thickness, and L is the thickness of the plate. In this case, the thermal conductivity, k, is the effective thermal conductivity of the composite perpendicular to the fiber axis. It was assumed that both the effective thermal conductivity and the effective density specific heat product, ρc_p,

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The problem described in eqs. (3.1a-d) can be solved numerically for the temperature distribution using the Crank-Nicolson finite difference method, given the thermal properties, and the initial and boundary conditions. The solution of the direct problem described here is inherent in the estimation of the thermal properties discussed in the following section.

3.1.2 Estimation of Thermal Properties

One method of estimating thermal properties involves the use of the Gauss minimization method. This method requires the solution of the temperature distribution as described in Section 3.1.1 and experimental temperature measurements within the composite specimen. The estimation method is based on a least squares function, S, which can be expressed mathematically as (Beck and Arnold, 1977)

$$S = \sum [Y - T(\beta)]^T [Y - T(\beta)] \qquad (3.2)$$

where the Y vector contains the measured temperature values, the T vector contains calculated temperature values, and the vector β contains the 'true' parameter values of thermal conductivity and density-specific heat. Given the appropriate experimental conditions, the calculated temperatures can be found from the solution of eqs. (3.1a-d).

In the Gauss method, as discussed in Section 3.4.1, the least squares function in eq. (3.2) is minimized with respect to β resulting in

$$\nabla_\beta S = 2[-X(b)][Y - T(b)] = 0 \qquad (3.3a)$$

where the sensitivity coefficient matrix, $X(b)$ is defined as $[\nabla_\beta T^T(b)]^T$, and the vector b contains the estimated parameter values. This equation can be rearranged to solve for b using an iterative scheme (Beck and Arnold, 1977), where

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$$b^{(i+1)} = b^{(i)} + (X^{T(i)}X^{(i)})^{-1}[X^{T(i)}(Y - T^{(i)})]$$ (3.3b)

In this equation, i indicates the iteration number, $b^{(i)}$ contains the parameters at the previous iteration, $b^{(i+1)}$ contains the new estimates for the parameters, and $T^{(i)}$ contains values of temperature calculated from $b^{(i)}$. The sensitivity coefficients in $X^{(i)}$ are found using a forward difference approximation for $X(b)$ about $b^{(i)}$. (If the number of parameters is greater than about three, the solution of the normal equations, eq. (3.3a), would be obtained by solving eq. (3.3a) directly rather than using the inverse implied in eq. (3.3b).)

An existing one dimensional parameter estimation program based on this procedure, *PROP1D* (Beck, 1987), was used in the estimation of thermal properties in carbon/epoxy composite materials. This program utilizes the concept of sequential estimation (Beck and Arnold, 1977), in which the parameters are evaluated at each (measurement) time step. This has one advantage in that one can observe the effects of additional data on the estimates of the parameters to evaluate the adequacy of the experimental design. Ideally, at the conclusion of an experiment, there should be no change in the parameter estimates with time; that is, any additional data would not effect the parameter estimates.

This program was used specifically to estimate the effective thermal conductivity perpendicular to the fiber axis and the effective density-specific heat of cured carbon/epoxy composites at different temperatures. The measured temperatures, Y, were obtained from experiments conducted at different temperatures as described in the experimental procedures in Chapter 4. The resulting estimates of these effective thermal properties at the different temperatures were then used to determine relationships between the thermal properties and temperature.

3.2 Estimation of Kinetic Parameters

In order to estimate thermal properties during curing, the heat generation due to the exothermic reaction of the epoxy must first be characterized. This analysis is based

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on the assumption that the heat of reaction rate is proportional to the degree of cure rate, thus enabling the use of differential scanning calorimetry (DSC) in determining the kinetic parameters which characterize the reaction. Due to the complexity of the curing process, several different kinetic models were investigated. these models can be separated into two groups: 1. limiting reaction rates due to autocatalyzation (degree of cure less than 50%); and, 2. limiting reaction rates due to diffusion (degree of cure greater than 50%).

3.2.1 Reaction Kinetics for Degree of Cure ≤ 50%

The kinetic models investigated for the initial curing phase of an amine-epoxy system are presented in eqs. (2.2), (2.4), and (2.5), and are again listed below.

$$\frac{d\alpha}{dt} = (c_1 + c_2 \alpha^m)(1 - \alpha)^n \qquad m + n = 2 \qquad (3.4)$$

$$\frac{d\alpha}{dt} = (c_1 + c_2 \alpha)(1 - \alpha)(B - \alpha) \qquad (3.5)$$

$$\frac{d\alpha}{dt} = c_1 (1 - \alpha)^n \qquad (3.6)$$

In all cases, the rate constants, c_i, are assumed to follow an Arrhenius relationship with temperature:

$$c_i = A_i \exp(-E_i / R(T + 273.15)) \qquad i = 1, 2 \qquad (3.7)$$

where, in this case, the temperature, T, is °C.

An autocatalyzed reaction was assumed in the models given by eqs. (3.4) and (3.5), and an nth order reaction was assumed in the model shown in eq. (3.6). By requiring the exponents m and n in eq. (3.4) to sum to two, a second order reaction is implicitly assumed in this model. The parameters to be estimated in each case are the activation energy constants, E_i, and the pre-exponential factors, A_i, and in addition, the two exponents, m and n, are to be determined for the models shown in eqs. (3.4) and

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(3.6), respectively. In the analysis of each of these models, the heat of reaction data are typically measured using differential scanning calorimetry (DSC) for several isothermal temperatures.

The underlying assumption in utilizing the DSC data for kinetic analysis, is that the cumulative heat of reaction is proportional to the reaction rate. The kinetic models discussed above require the fractional conversion (or degree of cure), α, as a function of time (assuming an isothermal cure), which can be obtained from the heat of reaction data as follows:

$$\alpha = \frac{\int_0^t H(t)dt}{H_t} \tag{3.8}$$

where H(t) is the heat of reaction at time, t, measured during isothermal DSC experiments, and H_t is the total heat of reaction from dynamic DSC experiments, given by

$$H_t = \int_0^{t_s} H(t)dt \tag{3.9}$$

where t_s is the total curing time. Dynamic DSC experiments are those in which the temperature is increased linearly with time throughout the entire cure. It is assumed in using this formulation that the total heat of reaction is independent of the curing temperature, even though at lower curing temperatures complete curing may not be achieved.

Kinetic parameters were determined for the first model (eq. 3.4) using two different methods. In both procedures, a second order reaction was assumed, so that $m + n = 2$, and the parameters estimated were A_1, A_2, E_1, E_2, and m. The first method to be described is that used by Ryan and Dutta (1979). In this case, the rate constant, c_1, was found by the initial degree of cure data; at the initial time, t, the degree of cure, α, is assumed to be equal to zero, and eq. (3.4) reduces to

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$$\frac{d\alpha}{dt}\bigg|_{t=0} = c_1 \tag{3.10}$$

The second rate constant, c_2, and the exponent, m, were found from the degree of cure at the maximum degree of cure rate, where the maximum is defined by

$$\frac{d^2\alpha}{dt^2} = 0$$

The expression for the degree of cure rate given in eq. (3.4) was differentiated with respect to time, and the resulting expression was set equal to zero, with $\alpha = \alpha_p$ as follows:

$$(2-m)c_1 \alpha_p^{1-m} + c_2 (2\alpha_p - m) = 0 \tag{3.11}$$

Solving eq. (3.11) for c_2 resulted in

$$c_2 = \frac{(2-m)c_1 \alpha_p^{1-m}}{m-2\alpha_p} \tag{3.12}$$

By substituting eq. (3.12) into eq. (3.14) with $\alpha = \alpha_p$ and rearranging terms, Ryan and Dutta obtained the following implicit relationship for m:

$$m\ln(\alpha_p) = \ln\left[\frac{\alpha_p'}{(1-\alpha_p)^{2-m}} - c_1\right] - \ln\left[\frac{(2-m)c_1 \alpha_p^{1-m}}{m-2\alpha_p}\right] \tag{3.13}$$

where α_p' is $(d\alpha/dt)$ evaluated at $\alpha = \alpha_p$. This equation was solved numerically for m, given values for c_1, α_p, and α_p' from DSC experiments at different temperatures.

Once the rate constants, c_1 and c_2 were determined for a few different isothermal cure temperatures, the activation energy constants and pre-exponential factors were found from eq. (3.7) using linear regression.

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Another method of determining the kinetic parameters in eq. (3.4) is presented here. The initial procedure is the same as that used by Ryan and Dutta (1979): m was estimated from c_1 and α_p using the initial degree of cure and the maximum degree of cure rate data. Equation (3.4) was then rearranged as

$$\frac{d\alpha/dt}{(1-\alpha)^{2-m}} = c_1 + c_2\,\alpha^m \qquad (3.14)$$

Equation (3.14) was solved for c_1 and c_2 using linear regression and the previously estimated values for m. This is an iterative procedure where m was recalculated from eq. (3.13) using the new value for c_1, and eq. (3.14) was again solved for c_1 and c_2. This procedure has the advantage that is uses all of the degree of reaction data, but it has the disadvantages in that all the parameters are not determined simultaneously and α and $d\alpha/dt$ are treated as if they are independent of each other.

In the second kinetic model (eq. 3.5), there are four parameters to be determined: A_1, A_2, E_1, and E_2. The rate constants were first determined using the procedure described by Sichina (DuPont Publ. No. TA-93); the kinetic equation was rearranged in a matter similar to that shown in eq. (3.14),

$$\frac{d\alpha/dt}{(1-\alpha)^2} = c_1 + c_2\,\alpha \qquad (3.15)$$

and, linear regression was used to determine c_1 and c_2. The activation energy constants and pre-exponential factors were then estimated using linear regression from the rate constants at different isothermal temperatures.

In the third model (eq. 3.6), an nth order reaction was assumed, and the parameters estimated were A_1, E_1, and the order of reaction, n. These parameters were estimated by first using linear regression to find the order of reaction, n, and the rate constant, c_1, for each temperature investigated. Then, A_1 and E_1 were found from the rate constants at different temperatures using linear regression.

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3.2.2 Reaction Models for Degree of Cure > 50%

Hawley et al. (1988) proposed the following model for a degree of cure greater than fifty percent. The basis of this model is the assumption that, as the epoxy cures and the number of cross-linkages increases, the flow of the molecules is restricted; therefore, the reaction is diffusion controlled. This is evident by the exponential decay term in the model:

$$\frac{d\alpha}{dt} = c_3 (1-\alpha)e^{-D\alpha} \qquad (3.16)$$

where the diffusion coefficient, D, and the rate constant, c_3, were found numerically using a nonlinear parameter estimation scheme. The rate constant was assumed to follow an Arrhenius relationship with temperature:

$$c_3 = A_3 e^{-E_3/RT} \qquad (3.17)$$

where A_3 and E_3 were found using linear regression (Scientific Programming Enterprises, 1987).

A modification of eq. (3.17) is presented here. It was based on the assumption that diffusion becomes significant at some value of extent of cure, say α equal to 50%. This value is designed as α_D as shown in the equation below,

$$\frac{d\alpha}{dt} = \left(\frac{d\alpha}{dt}\right)_{\alpha=\alpha_D} + c_3 (\alpha_D - \alpha)e^{-D(\alpha_D-\alpha)} \qquad (3.18)$$

Again, the unknown parameters, c_3 and D, were found using a nonlinear parameter estimation scheme (Scientific Programming Enterprises, 1987), and the activation energy constant, E_3, and the pre-exponential factor, A_3, were estimated from c_3 evaluated at different temperatures.

It should be noted that technically, neither of these models are true kinetic models, since by definition, diffusion is negligible in kinetic analysis; however, for these

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3.2.3 Selection of Kinetic Models for the Determination of Thermal Properties

Since it was assumed that the degree of cure rate was proportional to the heat of reaction of the composite during curing, the kinetic parameters were used in determining the heat generation due to the exothermic reaction of the epoxy. As shown in the following section, the amount of heat generated is necessary for the estimation of thermal properties during curing.

To determine the degree of cure rate throughout the curing process, one model was selected from the three models given for degree of cure less than 50%, and a second model was selected from the two models were presented for degree of cure greater than 50%. The selection of the models was based on the minimization of the 95% confidence intervals of the estimated parameters.

3.3 Estimation of Thermal Properties during Curing

The estimation of thermal properties of a composite during curing is similar to that described in Section 3.1 for estimating the thermal properties of cured composites. Several important differences must be noted, however. First, since the curing process is a result of an exothermic reaction, a heat generation term must be added to the energy equation shown in eq. (3.1a). This results in an additional differential equation, namely, the appropriate kinetic model (eq. 3.4), which must be solved along with the energy equation. Also, the thermal properties may be a function of degree of cure as well as temperature.

In this section, the direct problem of determining the temperature distribution resulting from heat conduction through a composite specimen during curing is defined, followed by a discussion of the solution method for the direct problem and the procedure for the estimation of the thermal properties.

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3.3.1 Heat Conduction in Carbon Fiber Reinforced Composites during Curing

One dimensional heat transfer was considered through a flat carbon-fiber/amine-epoxy reinforced composite plate during curing, with an imposed heat flux on one boundary and a known temperature history on the other boundary. It was assumed that the chemical reactions due to the curing of the epoxy generate heat within the composite plate at a rate proportional to the rate of extent of cure (Loos and Springer, 1983). A mathematical statement of this problem is

$$\frac{\partial}{\partial x}\left[k(T,\alpha)\frac{\partial T}{\partial x}\right] + \rho H_t\frac{d\alpha}{dt} = \rho c_p(T,\alpha)\frac{\partial T}{\partial t} \qquad 0 < x < L; \qquad t > 0 \qquad (3.19a)$$

with the boundary conditions,

$$-k(T,\alpha)\frac{\partial T}{\partial x} = q(t) \qquad\qquad x = 0; \qquad t > 0 \qquad (3.19b)$$

$$T = T_L(t) \qquad\qquad x = L; \qquad t > 0 \qquad (3.19c)$$

and the initial condition,

$$T = T_o(x) \qquad\qquad 0 \le x \le L; \qquad t = 0 \qquad (3.19d)$$

where x is the direction perpendicular to the fibers through the thickness, L is the thickness of the plate, ρ is density, and H_t is the total heat of reaction. In this case, the effective thermal conductivity (perpendicular to the fiber direction), k, and the effective density-specific heat, ρc_p, were assumed to be functions of temperature, T, and extent of cure, α. Once again, the heat flux, q, temperature, T_L, and the initial condition, T_o, were assumed to be known. The $\partial\alpha/\partial t$ term was obtained from the kinetic models selected for $\alpha < 50\%$ and $\alpha > 50\%$, as discussed in Section 3.2.3.

One method of solution involves the use of finite differences. At each time step, the appropriate kinetic equation (eq. 3.4 or eq. 3.18) can be solved using a forward difference approximation for the time derivative of α, and then the energy equation (eq.

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<u>3.3.2 Parameter</u>

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3.19a-d) can be solved using Crank-Nicolson approximations for the temperature derivatives. To simplify the solution, a quasi-linear approximation can be used to account for the temperature and extent of cure dependence of the thermal properties.

A one dimensional finite difference program, *CURE1D* (Appendix A), was written to solve the problem described by eqs. (3.19a-d) using the solution method described above. In the solution, eq. (3.4) and eq. (3.18) were selected for the kinetic models, and both the kinetic and thermal properties were assumed to be known. The thermal properties were assumed to be piecewise linear functions of temperature and extent of cure, for thermal conductivity, k:

$$k = k_{0_i} + k_{1_i}T + k_{2_i}\alpha \qquad T_i < T < T_{i+1}, \qquad \alpha_i < \alpha < \alpha_{i+1} \qquad (3.20)$$

where k is continuous at T_i and α_i, and k_0, k_1, and k_2 are constants obtained from known values of the thermal conductivity for a given temperature, T_i, and a given extent of cure, α_i. Equation (3.20) was written in terms of $k(\alpha_i,T_i)$, $k(\alpha_{i+1},T_i)$, and $k(\alpha_{i+1},T_{i+1})$ as follows

$$k = k(\alpha_i,T_i) + [k(\alpha_{i+1},T_i)-k(\alpha_i,T_i)](\alpha - \alpha_i)$$

$$+ \left[\frac{k(\alpha_{i+1},T_{i+1})-k(\alpha_{i+1},T_i)}{T_{i+1} - T_i}\right](T - T_i) \qquad (3.21)$$

A similar expression was obtained for the density-specific heat product. Using the quasi-linear approach, these parameters (k and ρc_p) were assumed constant over each time step.

3.3.2 Parameter Estimation Method

The parameter estimation procedure was similar to that described in Section 3.1.2 with the exceptions that the calculated temperatures in eq. (3.3) were obtained

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from the solution of eqs. (3.19a-d) instead of eqs. (3.1a-d), and the measured temperatures were obtained from a composite specimen during curing.

An updated version of the previously mentioned parameter estimation program, *PROP1DMA* (Beck, 1989), was modified to include the heat generation term shown in eq. (3.19a) due to the chemical reactions occurring during the curing of the epoxy. The modified program is called *PROP1D_CURE*. The same kinetic equations and solution technique used for the direct problem in *CURE1D* were also used in solving for the temperature distribution, T, in *PROP1D_CURE*.

3.4 Optimal Experimental Design Criterion for the Estimation of Thermal Properties

This section deals with the optimization of the experimental design for the estimation of the thermal properties of the composite material during curing. The objectives of the optimization are first presented, followed by a discussion of the development and use of the design criterion.

3.4.1 Objectives for the Experimental Design Optimization

One objective of this study was to estimate thermal conductivity and density-specific heat of carbon-epoxy composites during curing, with the assumption that these parameters are functions of temperature and extent of cure. In order to estimate thermal conductivity and density-specific heat independently, a heat flux boundary condition, such as that shown in eq. (3.19b), is required (Beck and Arnold, 1977). To simplify the estimation problem, it was desired to have short heat flux intervals with small temperature and extent of cure variations, compared to the overall temperature and extent of cure changes during the cure cycle, to justify the assumption of constant thermal properties over each heating interval. The objective here is to incorporate a number of these intervals at different degree of cure and temperature values in the experimental design so that a relationship between the thermal properties and degree of cure and temperature values can be obtained.

The recommended cure cycle for the AS4/EPON 828-mPDA composite system used in this study is for the specimen to be heated for two hours at 75°C and two hours at 125°C. Therefore, one objective for the experimental design was to have the heat flux interval be short compared to the overall curing time, and another was to have the temperature rise due the the heat flux be small compared to the temperature differentials in the curing cycle (e.g., 50°C). The third objective was that the heating interval be chosen to minimize the variance of the estimated thermal properties.

3.4.2 Optimal Experimental Design Criterion

The optimal experimental design criterion was based on the third objective listed above, with the first two objectives as constraints. In other words, a criterion was sought in which the heating interval duration time was optimized for the estimation of the thermal properties with the lowest variance, with the constraints that the interval be short compared to the total curing time and that the temperature rise during the heating time be small compared to temperature differentials in the recommended curing cycle. Practically, these constraints involved a fixed temperature rise and a fixed number of temperature measurements.

Many criteria have been proposed for the optimal design of experiments, and most of these involve the $\mathbf{X}^T\mathbf{X}$ matrix, where $\mathbf{X}$ is the sensitivity matrix. The criterion used here is recommended by Beck and Arnold (1977) because it is equivalent to the minimization of the hypervolume of the confidence region (for more than one parameter and for the standard statistical assumptions, Beck and Arnold, 1977). This criterion is the maximization of the determinant of the $\mathbf{X}^T\mathbf{X}$ matrix,

$$\Delta = |\mathbf{X}^T\mathbf{X}| \qquad (3.22)$$

Beck and Arnold (1977) presented an expression for Δ at time, t^n, where n is large and fixed, using uniformly spaced measurements, and two parameters. The expression for Δ for one sensor in dimensionless terms is

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where,

$$C_{ij}^+ = \frac{(T_{max}^+)^2}{t^n} \int_0^{t^{(n)}} X_i^+(t) X_j^+(t) dt, \qquad X_i^+(t) = \beta_i \frac{\partial T^+}{\partial \beta_i}$$

(3.23b,c)

and, $\qquad T_{max}^+ = \dfrac{T_{max}}{qL/k}$

(3.23d)

In these equations, T_{max} is the maximum temperature up to time, $t^{(n)}$, β_i is the ith parameter to be estimated, q is the heat flux, L is the thickness, and k is the thermal conductivity of the sample.

The heating time interval used in the transient temperature experiments during curing was determined using this criterion. The following hypothetical problem in dimensionless terms was formulated to simulate one heat flux interval during the experiments:

$$\frac{\partial^2 T^+}{\partial x^{+2}} + g^+ = \frac{\partial T^+}{\partial t^+} \qquad 0 < x^+ < 1 \qquad t^+ > 0;$$

(3.24a)

with boundary conditions,

$$-\frac{\partial T^+}{\partial x^+} = \begin{cases} 1 & 0 \le t^+ \le t_i^+ \\ 0 & t_i^+ < t^+ \end{cases} \qquad x^+ = 0; \qquad t^+ > 0;$$

(3.24b)

$$T^+ = 0 \qquad\qquad x^+ = 1 \qquad t^+ > 0;$$

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$$T^+ = 0 \qquad\qquad 0 \le x^+ \le 1 \qquad t^+ > 0;$$

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$$T^+ = \frac{T-T_\infty}{qL/k}, \qquad g^+ = gL/q, \qquad x^+ = x/L,$$

and

$$t^+ = \alpha t/L^2 . \tag{3.24e-h}$$

The heat generation term, g^+, was assumed to be constant over the heating interval. Note that the boundary condition at $x^+ = 1$ is $T^+ = 0$. This isothermal condition was chosen because the tested composite materials have low thermal conductivity and an approximate isothermal condition is relatively easy to simulate; it is done by attaching the specimen to a high thermal conductivity material. This is in contrast to estimating thermal properties of metals, which have relatively high thermal conductivity values. In such cases, the case of an insulated boundary condition at $x = L$ has been used (Beck and Arnold, 1977).

The temperature solution for the conditions given in eqs. (3.24a-d) was found for time, $t^+ < t_i^+$, as,

$$T^+(x^+,t^+) = 0.5g^+(1-x^{+2}) + (1-x^+) - 2\sum_{m=1}^{\infty} e^{-\beta_m^2 t^+} \cos(\beta_m x^+)(\beta_m - g^+(-1)^m)/\beta_m^3 \tag{3.25a}$$

and for $t^+ > t_i^+$,

$$T^+(x^+,t^+) = 0.5g^+(1-x^{+2}) - 2\sum_{m=1}^{\infty} \cos(\beta_m x^+)\left[(\beta_m - g^+(-1)^m)e^{-\beta_m^2 t^+} - \beta_m e^{-\beta_m^2 (t^+ - t_i^+)}\right]/\beta_m^3$$

$$\tag{3.25b}$$

The sensitivity terms in eq. (3.23b) were found by differentiating eqs (3.25a,b) with respect to the parameters thermal conductivity, k, and density-specific heat, ρc_p. Differentiating eq. (3.25a) first with respect to k resulted in the following expression for $t^+ < t_i^+$,

$$X^* = k\frac{2^?}{\sigma}$$

and for $t^* > t_1^*$,

$$X^* = -0.5$$

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$$X^* = -2$$

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$$X_t^+ = k\frac{\partial T^+}{\partial k} = -.5g^+(1-x^{+2}) - (1-x^+) + 2\sum_{m=1}^{\infty} e^{-\beta_m^2 t^+} \cos(\beta_m x^+)$$

$$\times(\beta_m - g^+(-1)^m)(1+\beta_m^2 t^+)/\beta_m^3 \qquad (3.26a)$$

and for $t^+ > t_i^+$,

$$X_t^+ = -0.5g^+(1-x^{+2}) + 2\sum_{m=1}^{\infty} \cos(\beta_m x^+)\left[(1+\beta_m^2 t^+)(1-g^+(-1)^m/\beta_m)e^{-\beta_m^2 t^+}\right.$$

$$\left. - (1+\beta_m^2(t^+-t_i^+))\, e^{-\beta_m^2(t^+-t_i^+)}\right]/\beta_m^2 \qquad (3.26b)$$

Equations (3.25a,b) were then differentiated with respect to ρc_p to obtain expressions for X_a^+. For $t^+ < t_i^+$,

$$X_a^+ = \rho c_p \frac{\partial T^+}{\partial k} = -2\sum_{m=1}^{\infty} t^+ e^{-\beta_m^2 t^+} \cos(\beta_m x^+)(\beta_m - g^+(-1)^m)/\beta_m \qquad (3.27a)$$

and for $t^+ > t_i^+$,

$$X_a^+ = -2\sum_{m=1}^{\infty} t^+ \cos(\beta_m x^+)\left[(1-g^+(-1)^m/\beta_m)e^{-\beta_m^2 t^+} - (t^+-t_i^+)(e^{-\beta_m^2(t^+-t_i^+)}\right] \qquad (3.27b)$$

To calculate the criterion Δ^+ in eq. (3.23a), the maximum temperature rise, T_{max}^+, was first determined from eqs. (3.25a,b) at $x^+ = 0$. The C_{ij} components in eq. (3.23b) were then found using numerical integration from T_{max}^+, and the sensitivity coefficients, X_t^+ and X_a^+, calculated using eqs. (3.26a,b) and (3.27a,b). Finally, the criterion, Δ^+, was found and compared for different heating intervals. Two different values of the dimensionless heat generation term, g^+, were used in analysis.

Results for the criterion of Δ^+ as a function of time for six different dimensionless heating times are shown in Figure 3.1 for $g^+ = 0.1$ and in Figure 3.2 for $g^+ = 1.0$. The

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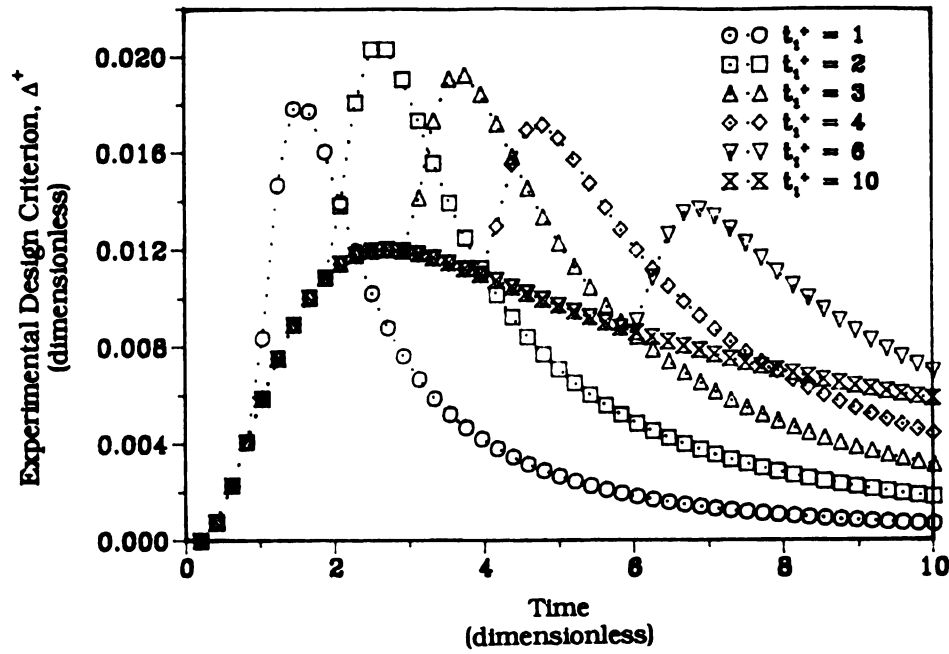
Figure 3.1 Dimensionless Experimental Design Criterion, Δ^+, for Different Dimensionless Heating Times, t_i^+, and a Dimensionless Heat Generation Term, g^+, equal to 0.1.
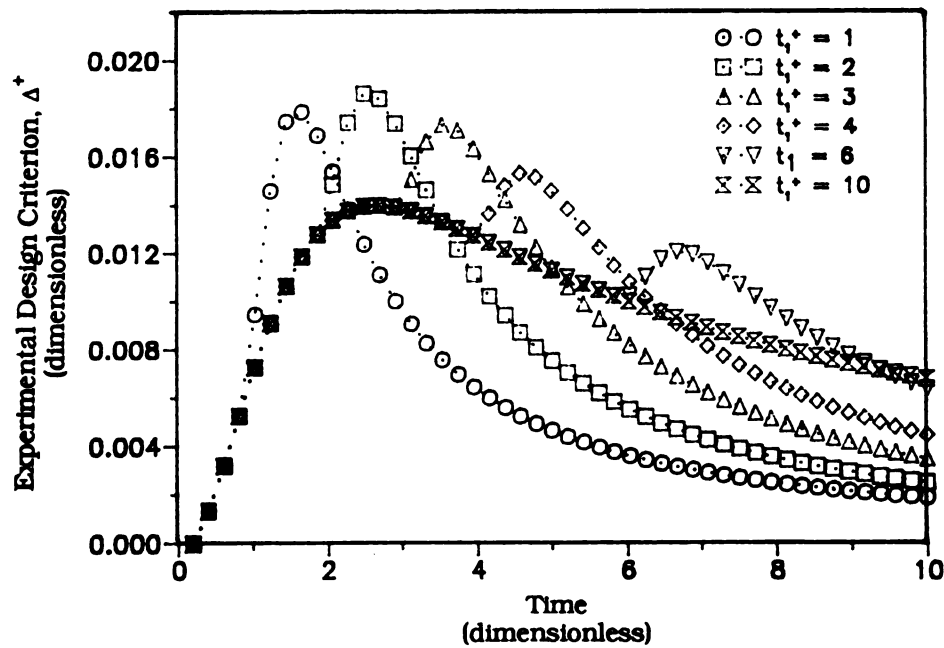
Figure 3.2 Dimensionless Experimental Design Criterion, Δ^+, for Different Dimensionless Heating Times, t_i^+, and a Dimensionless Heat Generation Term, g^+, equal to 1.0.

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optimum heating interval was chosen from the curve with the highest value of Δ^+. In both figures, the curves with the highest value of Δ^+ resulted from a dimensionless heating time, t^+, of 2. Further analysis of the case with $g^+ = 0.1$, revealed that the optimum heating time was closer to 2.125. An analysis of the case with $g^+ = 0.0$ indicated that the optimum heating time was approximately 2.25; therefore, the case for $g^+ = 1$, resulted in only a 10% decrease in the optimum heating time, compared to that with $g^+ = 0$.

The dimensional optimum heating time was determined from thermal property values based on results obtained for the cured composite samples from the analysis presented in Section 3.1 and a fixed thickness for the composite sample. The required heat flux was then calculated from eq. (3.23d), assuming a maximum temperature rise of no more than 5°C.

Chapter 4

Experimental Procedures

The focus of this chapter is on the experimental procedures used in the experiments used to estimate thermal and kinetic properties in carbon/epoxy composite materials. The first section is devoted to the procedures used in the transient temperature experiments for the estimation of thermal properties in cured composite materials (Section 4.1), and the second section is concentrated on the differential scanning calorimetry experiments used to estimate kinetic properties during curing (Section 4.2). In the final section, an outline of the methodology used in the transient experiments for the estimation of thermal properties during curing (Section 4.3) is given.

4.1 Experiments for the Estimation of Thermal Properties in Cured Composites

The experiments conducted for the estimation of thermal properties of cured composites involved temperature measurements within carbon/epoxy composite samples subject to an imposed heat flux at one boundary. These experiments are described in the following subsections. Included in these descriptions are the sample preparation techniques, the experimental set-up design, the data acquisition system, the procedures for the transient temperature experiments, and finally, a discussion of the experimental parameters.

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4.1.1 Preparation of the Composite Samples

The composite samples used in this study were composed of carbon fibers suspended in an epoxy matrix. All of the samples were prepared using the facilities in the M.S.U. Composite Materials and Structures Center. The preparation procedure can be divided into four phases: 1. epoxy preparation; 2. prepreg preparation; 3. stacking; and, 4. consolidation. In the first two phases, the two part epoxy was mixed, and then the carbon fibers were impregnated with epoxy (prepreg preparation). During the final two phases, stacking and consolidation, the prepreg plies or impregnated fibers were stacked and cured to form a composite plate. Each experimental set-up required the fabrication of four composite plates. The phases of the preparation procedure are described in detail in the following subsections.

4.1.1.1 Epoxy Preparation

The same type of epoxy was used in the transient experiments with cured composite materials, in the differential scanning calorimetry (DSC) experiments, and in the transient experiments during curing. The epoxy consisted of Shell's EPON 828 Resin with 1,3 Phenylenediamine (mPDA) as the curing agent, mixed in a one to one equivalency. The curing agent is a suspected carcinogen, so safety was a number one priority in the preparation procedures. The crystalline form of the mPDA is the most critical with regards to safety. Extreme caution was taken so that the crystalline form of the curing agent was not inhaled, and all skin contact with the mPDA was avoided. Therefore, a respirator, protective clothing, such as a laboratory coat, and disposable gloves were worn at all times during the preparation procedure. The protective clothing also served to protect one's personal clothing, since contact with the curing agent resulted in permanent stains. The detailed step by step procedure used to prepare the epoxy is given below.

1. The mPDA was set out at room temperature from cold storage at least one half hour before use.

2. Two large disposable beakers were cleaned with acetone, and then wiped dry with a disposable tissue.

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3. One of the beakers was tarred on a scale; the appropriate amount of resin was poured into the beaker (approximately 0.200 kg resin for prepreg preparation or 0.050 kg for DSC experiments); and, the weight of the resin was recorded.

4. The resin was then heated in an oven to approximately 70°C.

5. In the mean time, the second beaker was tarred, and the appropriate amount of mPDA was determined from the weight of the resin. For one to one equivalency, 0.0145 kg mPDA are required for every 0.100 kg epoxy (Rich, 1987). To measure out the appropriate amount of mPDA, the jar of mPDA was shaken with the lid on and placed on its side on some foil that was spread out in a fume hood. The jar was then opened, and the appropriate amount of mPDA was carefully scoped out into the second beaker using a clean spatula.

6. The beaker with mPDA was placed into the oven with the resin until the curing agent was completely melted (about 40 minutes). The mPDA was checked periodically, and stirred with a clean glass stirring rod if needed.

7. While mPDA was melting, the foil in the fume hood was removed, and the scale, the spatula, and the surfaces around where the curing agent was used were cleaned thoroughly with acetone. Both the foil and the cleaning cloths were placed in a sealed plastic bag for disposal.

9. The beaker with the resin was removed from the oven approximately five minutes before the mPDA was completely melted, and a vacuum oven was preheated to 60°C. Once the curing agent was melted, the resin was poured into the mPDA beaker, and the mixture was stirred until it appeared homogeneous. The epoxy mixture was placed into the vacuum oven (VWR Scientific, Inc. Model 1410), and the pressure was reduced to the limits of the instrument (-99 kPa). The mixture was held under a vacuum until bubbles on the side of the beaker had diminished (approximately 5 to 10 minutes); at that time, the epoxy mixture was removed, and the oven was turned off.

10. The epoxy mixture was then ready for immediate use in prepreg preparation or in DSC experiments.

4.1.1.2 Prepreg

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4.1.1.2 Prepreg Preparation

A prepreg consists of a single layer of fibers impregnated with uncured resin. In this study, the prepregs were prepared from EPON 828/mPDA epoxy resin and continuous AS4 carbon fibers with 12,000 fibers per tow (Hercules Aerospace Corp.); all of the prepregs were prepared using carbon fibers from the same lot number (Lot No. 708-4C). A hot-melt prepregger (Research Tool Co.) was used to impregnate the fibers with the resin to form a prepreg. In this procedure, a tow of continuous fibers was fed through a small vat of epoxy and then through a die, so that the tow was completely impregnated with fibers. The tow was then wrapped around a drum to form a prepreg. The epoxy resin was prepared using the procedure described in Section 4.1.1.1, and the detailed procedure to impregnate the fibers with the resin is given below. The Research Tool Corporation Prepregger is shown in Figure 4.1. Additional views of the prepregger, indicating the parts referenced in this section, are shown in Figures 4.2-4.6. Once again, protective clothing and disposable gloves were worn.

1. While the mPDA was melting (step 7., Section 4.1.1.1), the prepregger was prepared. First, a spool of AS4 carbon fibers was placed on the single spool mount and secured in place using the large spool holder, the side mounting bracket, and the end nut. The side bracket was held in place with two thumb screws. The single spool mount with the spool of fibers in place is shown in Figures 4.2a,b.

2. A tow, or strand of fibers, was then fed up over the first guide roller, through the furnace (which was not used), and around the tension rollers, as shown in Figures 4.3a,b.

3. The resin pot chamber was fastened in place with two thumb screws. The tow was then guided through the resin pot, and the exposed layer of the fiber on the spool was pulled off and thrown away. Masking tape was used around the ends prior to cutting.

4. The large end of the die appropriate for this fiber (die A-A) was placed under the resin pot, and secured in place with a thumb screw. The control panel of the prepregger was then turned on, and full tension was applied to the fiber. The tow
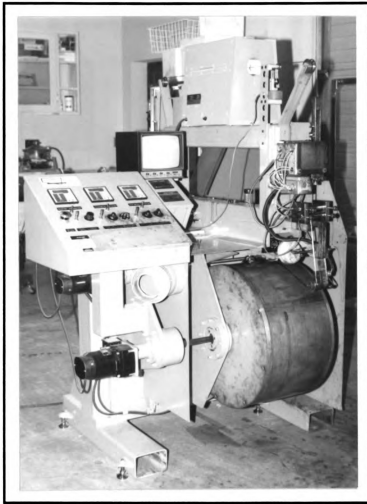
Figure 4.1 Hot Melt Prepregger (Research Tools Corporation).
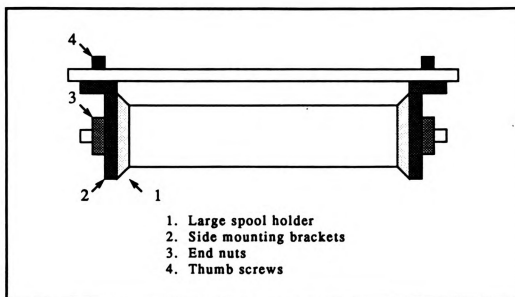
Figure 4.2a   Schematic of Single Spool Mount on Hot-Melt
Prepregger.
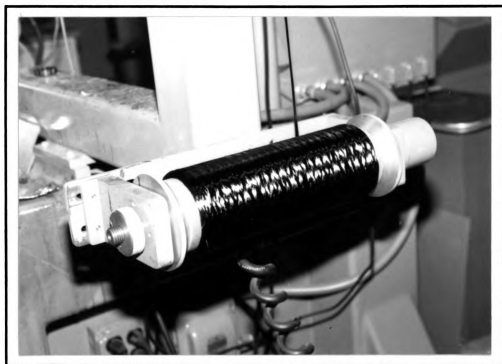
Figure 4.2b Photograph of Single Spool Mount.
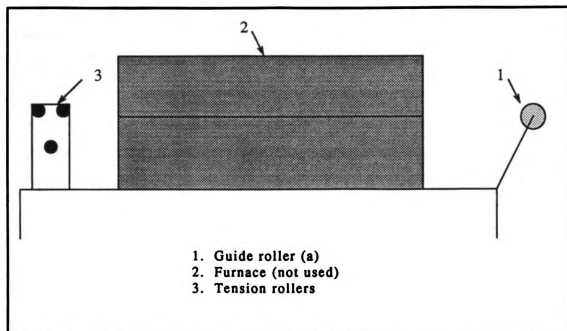
Figure 4.3a Schematic of Guide Roller, Furnace, and Tension
Rollers on Hot Melt Prepregger.
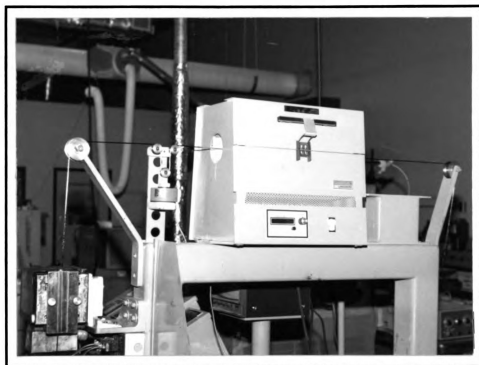
Figure 4.3b Photograph of Fibers Through Guide Roller, Furnace,
and Tension Rollers.

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was pulled taut against the die opening so that all of the fibers were in the die opening. The small end of the die was then put in place with a thumb screw, taking care to keep the tow taut. Two large thumb screws were then used to secure both ends of the die. Extreme care was taken not to pull on the dry tow once the die was in place, since this would break the fibers. The die, mounted on the resin pot, with the fibers in place is shown in Figures 4.4a,b, and a close-up view of the resin pot, die and pin guide (step 7) is shown in Figure 4.5.

5. The resin pot, flattening pin, and guide roller heaters (Figures 4.4a,b) were then turned using the control panel (Figure 4.6). The set points were adjusted as follows:

Resin pot = 125°F (69.4°C)

Flattening pin = 95°F (52.8°C)

Guide roller = 95°F (52.8°C)

6. Two sheets of plastic, 193 cm by 33 cm, were cut. The plastic was used to prevent the impregnated tow from sticking to the drum and to protect it from outside contamination. One end of one sheet was taped to the prepregger drum (Figures 4.4a,b), and the drum was rotated so that the plastic lay smoothly on the drum. The remaining end was then taped down, and then the plastic was cleaned thoroughly with acetone.

7. Once the epoxy mixture was ready (see step 10, Section 4.1.1.1), the mixture was poured into the resin chamber until it was about two-thirds full. Some epoxy was poured over the fibers above the resin pot to ease the placement of the pin guide. The pin guide was then inserted so that the fibers ran in front of the top pin, behind the second, and in front of the bottom two pins. The guide was placed so that the top pin lay just below the surface of the resin pot, and it was secured in place with a side mount and two thumb screws (Figure 4.4a,b).

8. Once the pin guide was set in place, the resin chamber was filled up to the rim with epoxy.

9. The tension on the fibers was released, and the wetted tow of fibers were pulled down through the die, between the flattening pins, and around the guide

1. Resin pot chamber
2. Die (A-A)
3. Guide pin
4. Flattening pin
5. Guide roller (b)
6. Drum

(b) photograph
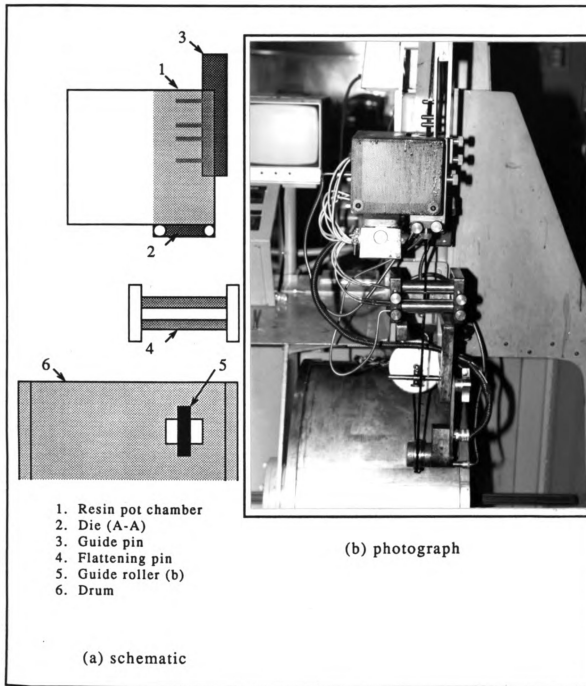
(a) schematic

Figure 4.4a,b Schematic (left) and Photograph (right) of Resin Pot Assembly
on Hot Melt Prepregger.
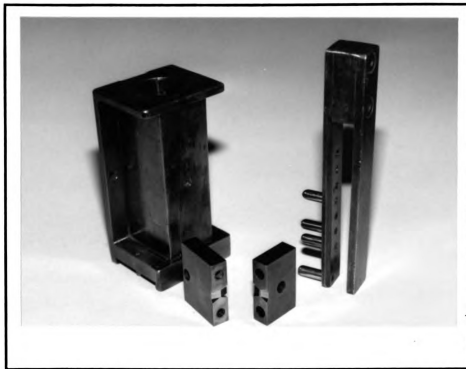
Figure 4.5   Detailed View of Resin Pot, Die (A-A), and Pin
Guide (from left to right).

Figure 4.6 Hot-Melt Prepregger Control Panel.

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roller. The tow was then taped to the drum, and the drum was rotated at least one half revolution to ensure that the tow stayed in place.

10. The drum rotation, fiber tension, and drum carriage movement controls were adjusted as follows:

> Drum rotation - 1.0 rpm
>
> Fiber tension - 0.5 to 1.0
>
> Drum carriage movement - approximately 23 (scale: 0 to 100)

The fibers were watched carefully for the first three to four revolutions, and the carriage movement was adjusted so that in each rotation, the tow lined up the previous rotation with no gaps between the two lines.

11. The resin pot was checked and refilled every five to ten minutes to keep the resin level above the top guide pin.

12. When the fiber had wound to the left hand side of the drum, the drum rotation and drum carriage movement were turned off, and the fiber was cut off close to the drum.

13. The remaining sheet of plastic was cleaned with acetone, and one end was placed on the surface of the exposed fibers. The drum was rotated slowly, and the plastic was wrapped smoothly around the drum. The prepreg was cut away from the drum along a grooved cutting line using a utility knife with a new blade.

14. The prepreg was then carefully rolled or folded, and placed in a sealed plastic bag in a freezer until needed.

15. The clean up process was critical in this procedure since the epoxy mixture can eventually cure and harden at room temperature. The clean up procedure is given below.

> a. The fiber around the resin pot was cut off and discarded. The resin pot was then removed by unscrewing the two thumb screws on the side of the pot, and the remaining resin in the pot was drained into the resin beaker under the fume hood.
>
> b. The prepregger was cleaned thoroughly with acetone, especially around the resin pot chamber. The flattening pins were cleaned in place, but the

guide roller was removed and cleaned under the hood. The drum was also cleaned with acetone, and excess tape was removed.

c. All switches on the control panel were turned off, along with the power switch to the control panel.

d. The spool of fiber was wrapped in foil, labeled, and put away.

e. The screws, pin guide, and die were removed from the resin pot under a fume hood. All pieces were carefully washed twice with acetone, and placed back on the prepregger.

f. Finally, the fume hood area was checked and cleaned with acetone, and the soiled cleaning cloths and empty beakers were sealed in a plastic bag and disposed of properly. The epoxy in the resin beaker was allowed to cure in the hood at room temperature before discarding.

4.1.1.3 Stacking Procedure

The prepreg plies were stacked and prepared for curing in this phase. Twenty-four pieces or plies were cut from the prepreg and stacked for each composite plate. In stacking the prepreg plies, two fiber orientations were used: $[0°]_{24}$ (parallel fibers) and $[0, 30, -30, 60, -60, 90°]_{2(sym)}$ (quasi-isotropic laminate). The two stacking orientations are shown in Figure 4.7. One prepreg was required for each of the $[0°]_{24}$ composite plates, and one and a half prepregs were required for each of the quasi-isotropic plates. A total of eight $[0°]_{24}$ and four $[0, 30, -30, 60, -60, 90°]_{2(sym)}$ plates were prepared. After stacking, the prepreg laminates were placed on an aluminum plate covered with a piece of release ply, which is a plastic sheet used to protect the aluminum plate from the epoxy. A dam was built up around the composite using a gummy tape or a cork tape to maintain the shape of the laminate during consolidation. Pieces of porous Teflon^R cloth and bleeder cloth were then placed on top of the composite. The bleeder cloth is an absorbent material used to absorb the excess epoxy during consolidation, and the porous Teflon^R cloth was placed between the prepreg laminate and the bleeder cloth to protect the surface of the composite. A second aluminum plate, covered with a release ply was laid on top of the bleeder cloth, and then the entire assembly was sealed in a
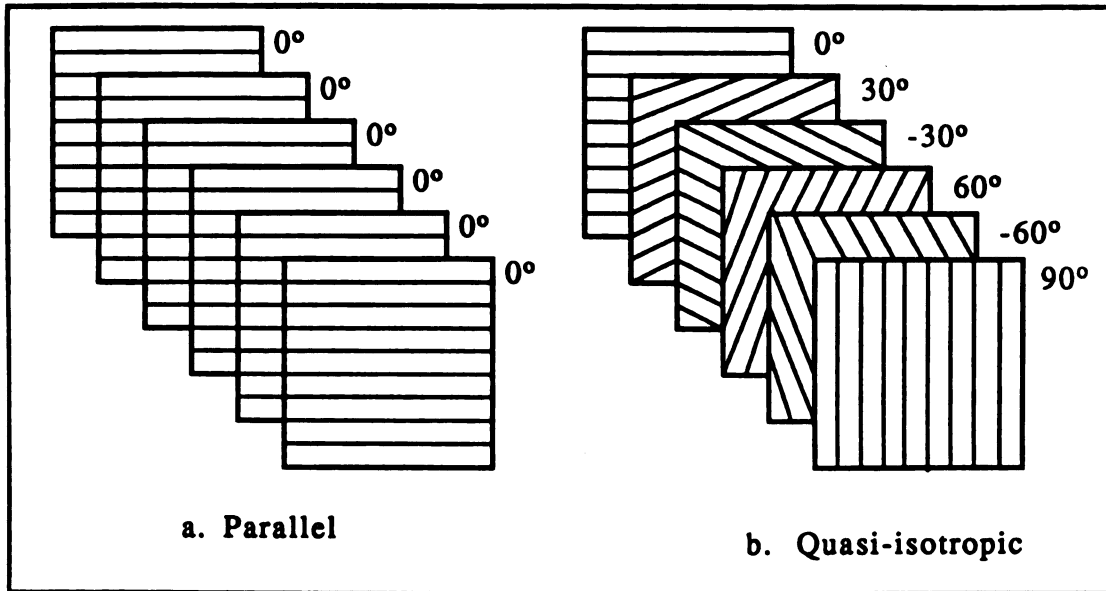
Figure 4.7 Stacking for Orientation for the First Six Parallel and the
First Six Quasi-isotropic Laminates for the $[0°]_{24}$ and the
$[0°,30°,-30°,-60°,60°,90°]_{2(sym)}$ Composite Disks.

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vacuum bag for curing. The steps used in the stacking process for one plate are as follows.

1. One 23 cm by 23 cm square piece was cut from the porous Teflon^R cloth and from the bleeder cloth, and two 23 cm by 23 cm squares pieces were cut from the release ply. In addition, a small piece of thick bleeder cloth (approximately 8 cm by 10 cm) and sheet of vacuum bag material at least 40 cm by 70 cm were cut.

2. The prepreg was taken out of the freezer and allowed to cool just enough to become pliable (approximately 5 minutes); during this time, approximately 3 kg of dry ice was obtained and chopped into small chunks.

3. The prepreg, which measured 193 cm by 30.5 cm, was spread out on a sheet of foil, and a piece of poster board was placed under the section to be cut. Using a carpenters square as a guide and a sharp utility knife, twenty-four 15.2 cm by 15.2 cm plies were cut from each prepreg for the $[0°]_{24}$ composite plates. Since the prepreg had to be cut at different angles for the quasi-isotropic plates, one and a half prepregs were required for each of these plates.

4. One piece of the release ply was secured using to a smooth 23 cm by 23 cm square aluminum plate using small amounts of Tacky Tape^R (Schnee-Morehead, Inc.) at the corners.

5. The dry ice was used to facilitate the removal of the release ply from the prepreg. Several prepreg plies were laid out on the foil, and the remainder plies were placed back in the freezer until needed. Using thermal gloves, the dry ice was spread over the prepreg plies, and the release plies on one side of each ply were peeled off as they stiffened and separated from the prepreg. Particular attention was taken not to peel off any fibers with the plastic. After any accumulated frost on the exposed surface had evaporated off, two prepreg plies were stacked together with the desired fiber orientation ($[0°]_{24}$ or $[0, 30, -30, 60, -60, 90°]_{2(s \, y \, m)}$). A roller was used to press the plies together in an effort to remove air trapped between the plies.

6. Step 5. was repeated with all 24 plies, resulting in a 24 ply laminate with two release plies still in tack.

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7. One of the last two release plies was then removed, and the laminate was placed face down on one of the aluminum plates covered with release ply.

8. Either gummy tape (Air Dam I, General Sealants) or 0.32 cm (or 0.16 cm) by 2.54 cm cork tape (Pressure Sensitive Backed Cork Dam, Northern Fiber Glass Sales, Inc.) was used to as a dam around the sample. The dam was built up until it was level with the laminate thickness.

9. The last release ply was removed from the sample, and the exposed surface was covered with the porous Teflon^R cloth, followed by the bleeder cloth and the second aluminum plate protected with release ply.

10. The entire assembly was centered on one half of the sheet of vacuum bag material. A rubber hose was held in place with Tacky Tape^R at one end of the vacuum bag, with the piece of thick bleeder cloth placed over the mouth of the tube towards the inside of the bag. The remaining vacuum bag material was folded over the assembly, and then Tacky Tape^R was used around the edges to seal the bag. The assembly was checked visibly for leaks, and extra tape was added where needed, especially around the rubber tube. A diagram of the stacked prepreg is shown in Figure 4.8. The prepreg laminate was then ready for consolidation.

4.1.1.4 Consolidation

The prepreg laminates were consolidated either in an hydraulic press with heated platens (Fred S. Carver, Inc., Hydraulic Equipment, Model SP-F-6030) or in an autoclave (United McGill Corporation). The eight $[0°]_{24}$ plates and two of the quasi-isotropic plates were cured in the press; the remaining two quasi-isotropic plates were cured in the autoclave. (The autoclave was not available at the time the first ten samples were made.) The same curing cycle was used in both cases. Pressure was applied so that the pressure over the surface of the laminate equaled 689 kPa (100 psi), and the laminate was heated to 75°C at 5°C/min. During this time, the hose on the vacuum bag was attached to a vacuum pump, and pressure inside the base was reduced to -99 kPa. This was done to further remove any air which might have been
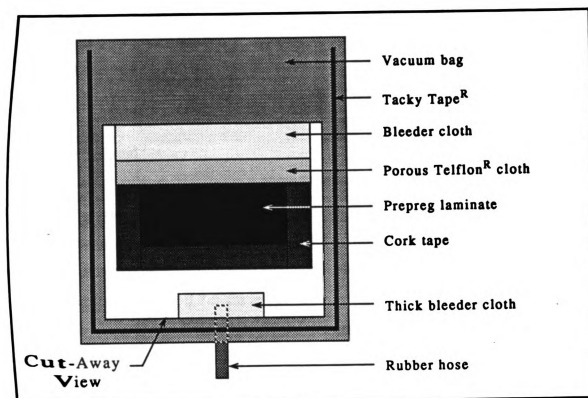
Figure 4.8   Cut-Away View of Stacked Prepreg Laminate.

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trapped between the prepreg plies. The laminate was held at 75°C for two hours, then it was heated to 125°C at 5°C and held at 125°C for another two hours, according to the recommended curing cycle for this composite (Rich, 1987).

After completion of the cure cycle, the composite laminate plates were cooled down to room temperature, and then they were taken out of either the press or the autoclave, removed from the vacuum bag, and separated from the stacking materials. At this time the plates, measuring approximately 15.2 cm by 15.2 cm by 3 to 4 mm in thickness, were ready for use in the experimental set-ups, described in the next section.

4.1.2 Experimental Set-up

Two experimental set-ups were assembled using the eight $[0°]_{24}$ composite disks, and a third experimental set-up was assembled using the four $[0, 30, -30, 60, -60, 90°]_{2(sym)}$ disks. Each experimental set-up was composed of four disks cut from the composite plates, a resistance heater, thermocouples, and two aluminum cylinders.

The disks, measuring 7.6 cm in diameter, were cut from the center of each plate to avoid any end effects resulting from the stacking process. The thickness of each disk was measured at various locations around the disk and recorded; a record of the average thickness, consolidation method, and fiber orientation for each disk is given in Table 4.1. The variations in the thicknesses between disks cured in the hydraulic press were most likely a result of differences in the applied pressure, which could not be controlled accurately. (Due to the hydraulic control on the press, the pressure was maintained at a constant value throughout the curing process; however, the pressure was initially set with an accuracy of only ± 2 kPa.) The greater thicknesses reported for the samples cured in the autoclave were most likely due to the use of the cork tape as a damming material instead of the gummy tape. The cork tape proved to be a better containment material for the epoxy than the gummy tape due to its more rigid form. (The cork tape was not available at the time the first eight samples were fabricated.)

The resistance heaters were thin (0.25 mm), 7.6 cm diameter, 9.4 ohm Thermofoil[R] heaters (Minco Products, Inc.) and were used to provide the heat flux boundary condition shown in eq. (3.1b). The thermocouples were fabricated from

Table 4.1 F
Experiments.

Disk No.	T...
1	2
2	3.
3	3.
4	4.
5	3.
6	3.
7	3.
8	3.
9	3.
10	3.
11	4.
12	4.

a. Cork tape

Table 4.1   Fabrication Parameters for Cured Composite Disks used in Transient Experiments.

Disk No.	Thickness (mm)		Consolidation Method	Fiber Orientation
	mean	st.d.		
1	2.96	0.04	hydraulic press	$[0°]_{24}$
2	3.32	0.05	hydraulic press	$[0°]_{24}$
3	3.56	0.02	hydraulic press	$[0°]_{24}$
4	4.17	0.10	hydraulic press	$[0°]_{24}$
5	3.02	0.11	hydraulic press	$[0°]_{24}$
6	3.01	0.11	hydraulic press	$[0°]_{24}$
7	3.68	0.08	hydraulic press	$[0°]_{24}$
8	3.66	0.03	hydraulic press	$[0°]_{24}$
9	3.14	0.07	hydraulic press	$[0,30,-30,60,-60,90°]_{2(sym)}$
10	3.56	0.09	hydraulic press	$[0,30,-30,60,-60,90°]_{2(sym)}$
11	4.61	0.04	autoclave[a]	$[0,30,-30,60,-60,90°]_{2(sym)}$
12	4.93	0.02	autoclave[a]	$[0,30,-30,60,-60,90°]_{2(sym)}$

a.   Cork tape used as a dam instead of gummy tape.

chromel and constantan wires (ANSI Type E). The two aluminum cylinders, each with a diameter of 7.6 cm and a height of 3.7 cm, were used to as heat sinks to approach a constant temperature for the boundary condition shown in eq. (3.1c). The procedures used in fabricating the thermocouples and in assembling the experimental set-up are given in the following subsections.

4.1.2.1 Thermocouple Fabrication

Fine thermocouples were used in both the transient temperature experiments on cured composite samples and the experiments on composite samples during curing. The thermocouples were prepared from 0.08 mm (AWG 40), chromel/constantan (ANSI Type E), Teflon^R/Neoflon^R duplex insulated wires from Omega Engineering, Inc. The duplex insulation consisted of an inner insulation layer around each individual wire, plus an outer insulation layer around both wires.

To prepare each thermocouple, the thermocouple wire was cut into pieces approximately 94 cm long, and the outer insulation layer was stripped off 40 cm from one end. The inner insulation layer around each wire was stripped off about 8 cm from the same end, and pieces of overbraid insulation, approximately 32 cm long, were slipped over each wire to cover the portion of the wire with only one layer of insulation. The exposed wires were flattened to approximately 0.05 mm by placing them between smooth, flat, steel dies and applying pressure using a hydraulic press. The flattened ends of the wires were over-laid and welded using a portable welder (Black & Webber, Model 848). The other end of the thermocouple was stripped about 1 cm from the end, and instrumented with a male, Type E, subminiature thermocouple connector from Omega Engineering, Inc. A prepared thermocouple with a close up view of the thermocouple junction is shown in Figure 4.9.

In addition, extension thermocouple wires were used to connect the instrumentation thermocouples to the data acquisition system. PFA Teflon^R Coated ANSI Type EX extension grade wires with 304 stainless steel shielding (Omega Engineering, Inc.) were used for this purpose. Female subminiature connectors were placed on one end for connection with the instrumentation wire, and the other end was either stripped for

Close-up view of Thermocouple
Junction
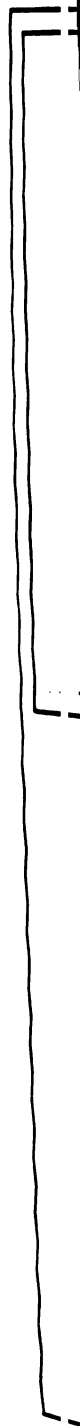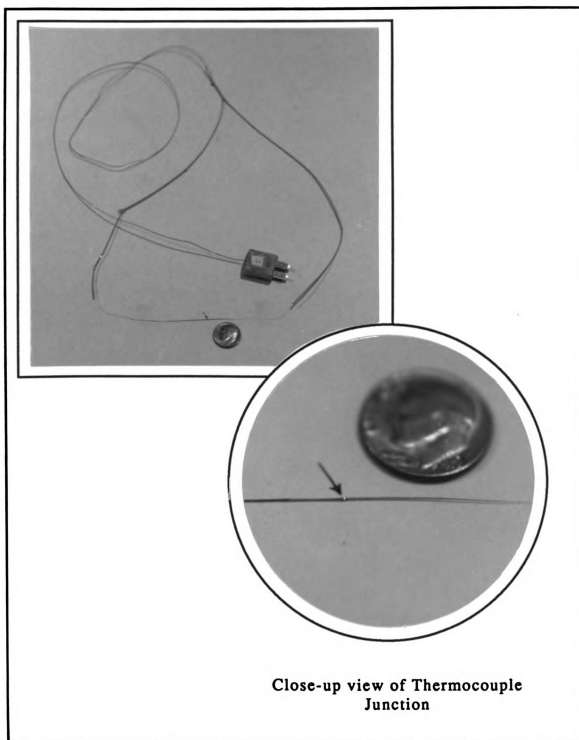
Figure 4.9 Prepared Thermocouple (ANSI Type E) with Close-up View of
Thermocouple Junction.

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direct connection to the data acquisition system or fitted with male subminiature connectors.

4.1.2.2 Experimental Set-up Assembly

The composite disks were stacked with two thermocouples laid in between each plate. The thermocouples were placed across the disk about 6 mm on either side of the center line of the disk perpendicular to the fibers, with the thermocouple junction on the center-line of the disk parallel to the fibers. A diagram of the thermocouple placement on one disk is shown in Figure 4.10. For the set-ups with parallel fibers, the disks were placed on top of one another with the fibers on one disk parallel to the fibers on the adjacent disk. In the case of the set-up using the disks with the $[0, 30, -30, 60, -60, 90°]_{2(sym)}$ fiber orientation, the disks were arranged so that the fibers on the two adjacent surfaces were parallel to provide symmetry. Silicon grease (Silicon Heat Sink Compound, Dow Corning Corp.) was used to provide good thermal contact between the plates and between the thermocouples and the plates. This grease was applied to one side of each disk before placing the thermocouples using a small, thin, flat board. The silicon was spread out down until its thickness appeared uniform, with no gaps or clumps.

A resistance heater was placed between the middle two disks, and two additional thermocouples were placed on each side of the heater, again using the silicon grease between the heater and the composite plates. The disks were stacked so that the total thickness on either side of the heater was approximately equal. The stacked composite disks instrumented with thermocouples and the resistance heater, were then placed between the two aluminum cylinders, and two thermocouples were placed at each of the composite disk-aluminum cylinder interfaces. The entire assembly was then pressed together between two 14 cm by 14 cm by 4 mm aluminum plates. Pressure was applied through threaded rods which ran through the corners of the aluminum plates. A photograph of the experimental set-up is shown in Figure 4.11.

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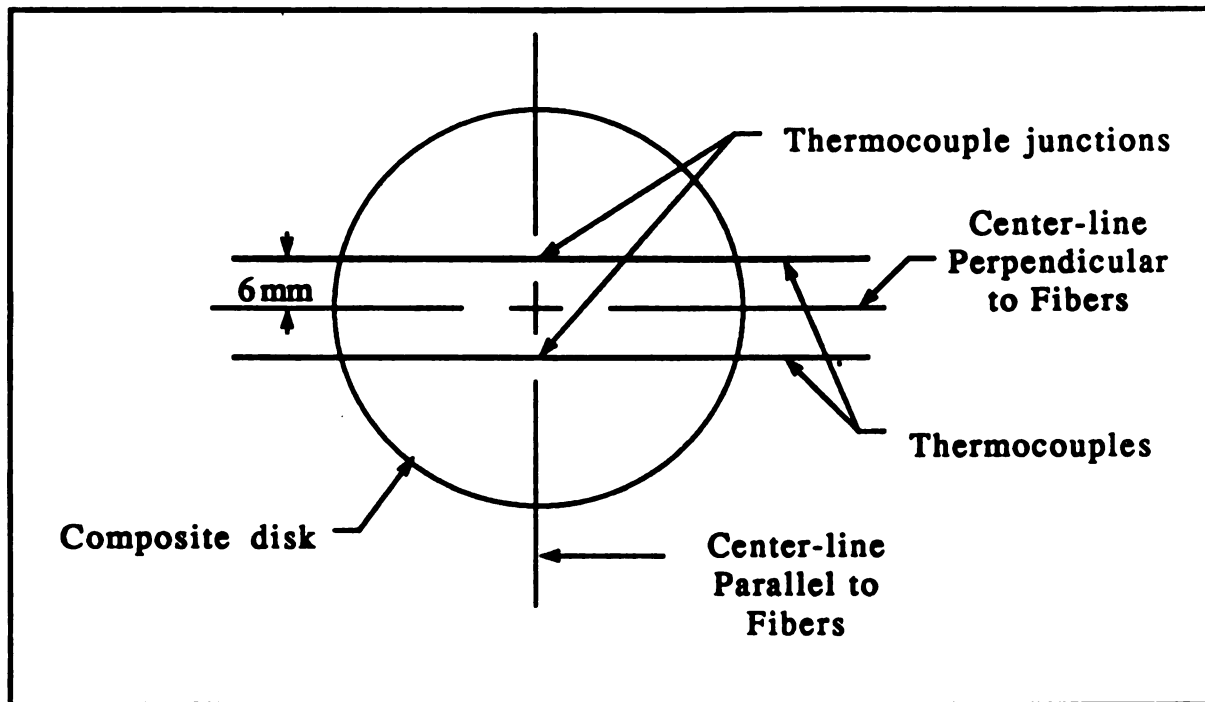
Figure 4.10 Thermocouple Placements on Composite Disks Used in Transient Temperature Experiments.
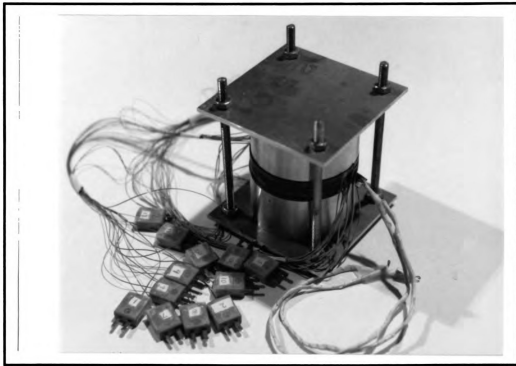
Figure 4.11 An Experimental Set-up for Transient Temperature
Measurements using Cured Composite Samples.

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4.1.3 Data Acquisition System and Controlled Heat Flux

Temperature measurements from the thermocouples were recorded using a PDP 11/05 microcomputer (Plessey Peripheral Systems) running under an RT-11/V4 operating system. The signal from the thermocouples was conditioned through the use of amplifiers prior to being read by the RT-11/V4 system. The data acquisition hardware, signal conditioning, and data acquisition software are described in the following sections. A schematic of the data acquisition system and power supply for the controlled heat flux is shown in Figure 4.12.

4.1.3.1 Data Acquisition Hardware

The PDP 11/05 was equipped with an analog-to-digital (A/D) converter (Model DT2764) and a real-time clock/counter unit (Model DT2769). Both of these units were supplied by Data Translation, Inc. The full scale input voltage on the A/D converter was configured to operate from 0 to 10 V, with a gain of one and with eight differential ended input channels. The clock unit was a programmable unit which determined the intervals of count events. Details of these devices are given by Osman (1987).

4.1.3.2 Signal Conditioning

Since the signal produced by the thermocouples was on the order of millivolts and the A/D operated on a scale from 0 to 10 V, a signal conditioning unit was required to amplify the thermocouple signals prior to processing by the A/D converter. This unit, also supplied by Data Translation, Inc., consisted of a ±15 V power supply (Model DT7692), a backplane board (Model DT750), and eight amplifiers (Model DT6705E).

Each amplifier was instrumented with an electronic cold junction compensation for ANSI Type E thermocouples. In this case, the extension thermocouple wires were connected directly to the channel trip on the DT750 backplane. The gain of the amplifiers was set at 1000, and before each experiment, the zero calibration was adjusted using the calibration screws on the front panel of each amplifier.
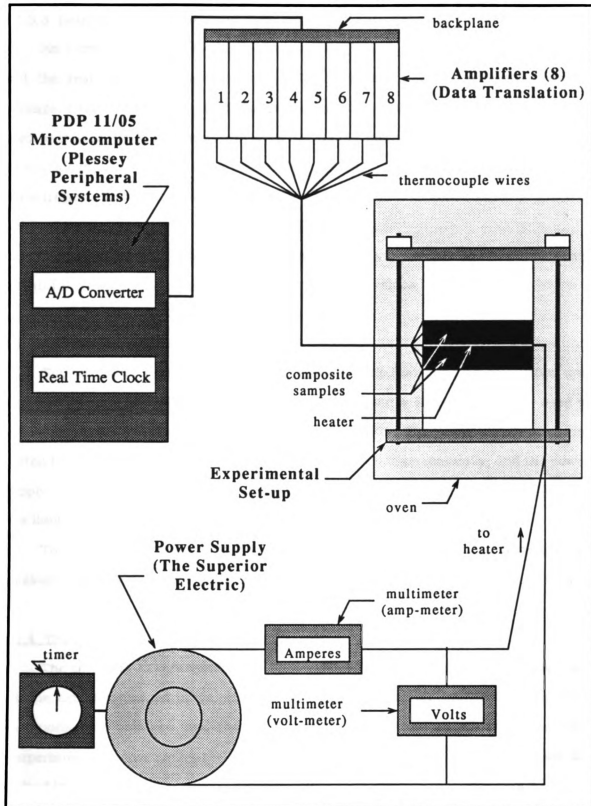
Figure 4.12 Schematic of Data Acquisition for Transient
Experiments using Cured Composite Samples.

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4.1.3.3 Data Acquisition Programs

An existing program, *DATACQ* (Osman, 1987), was used for controlling the A/D and the real-time clock-counter units. The program utilizes a real-time software package, *DTLIB/RT*, provided by Data Translation, Inc. (1981). The real-time clock was used to trigger the A/D converter at user designated intervals. The A/D operated in a 'sweep' mode, in which the input channels 0 through 7 were read sequentially on each clock trigger. The time required for each sweep was less than 0.002 seconds (Osman, 1987).

An adjoining program, *DATFIT* (Osman, 1987), was used to convert the binary output from the thermocouple readings to temperature values.

4.1.3.4 Controlled Heat Flux

The resistance heater was controlled independently from the data acquisition system. A Powerstat[R] Variable Autotransformer (The Superior Electric, Co.) was used to supply the power requirements for the resistance heater. The power supply was connected to a timer; during operation, the timer was switched on manually, and the power supply was activated for a preset interval on the timer. The maximum heating interval was limited to 60 seconds using this timer.

To measure the applied heat flux, two multimeters (Keithley Co.) were used to measure the current to the heater and the voltage drop across the heater (Figure 4.12).

4.1.4 Transient Temperature Experiments

The transient experiments using the cured composite samples consisted of placing the experimental set-up in an oven at the desired temperature until steady-state conditions were obtained, and then activating the heater and recording the resulting temperature response using the data acquisition program. The procedures used for each of these experiments were as follows:

1. The experimental assembly was placed in an oven; then the thermocouples

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were connected to the extension cables wired to the backplane of the data acquisition system; the heater was wired to the power supply; and, the assembly was heated to the desired testing temperature (this usually took two to three hours).

2. The data acquisition program was started, and the experimental parameters, such as sampling rate, total experimental time, and number of thermocouples, were entered. The total heating time was set on the timer connected to the power supply.

3. Data acquisition commenced upon an external input to the data acquisition program. At the same time the data collection was started, a stop watch was activated. The heater was manually started 20 seconds after each experiment was begun, and the voltage and amperage readings were recorded every five seconds for the duration of the heating interval. Data collection continued on the data acquisition program until the end of the total experimental time.

4.1.5 Experimental Parameters

The experimental parameters in the transient temperature experiments using cured composite materials included total experimental time, data sampling interval, ambient temperature, heating time interval for the resistance heater, magnitude of the heat flux, fiber orientation with respect to heat flux, number of thermocouples and the total number of repetitive experiments for each set of parameters.

The total experimental time was set at 200 seconds, with a one second data sampling interval for all cases. The experiments were conducted at five different ambient temperatures: 25 (or room temperature), 50, 75, 100, and 125°C. The ambient temperature conditions above 25°C were conducted using the oven as described in Section 4.1.4. These temperatures served as the initial temperatures for each run since the resistance heater heated the composite samples above these temperatures.

The heating time interval was set at 40 seconds, using the timer connected to the Powerstat^R power supply, and the output power from the power supply was adjusted to about 28-29 watts. This resulted in a maximum temperature rise of approximately 15 to 20°C above the initial temperature.

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The fiber stacking angles investigated were $[0°]_{24}$ and $[0, 30, -30, 60, -60, 90°]_{2(sym)}$, as discussed previously. This study was limited to the estimation of the thermal properties transverse to the fiber direction, so in all cases the heat flux was assumed perpendicular to the fiber axis. Therefore, it was anticipated in this case that similar results would be obtained for the two different fiber stacking angles. It should also be noted that the orientation of the fibers is only pertinent with respect to the estimation of the effective thermal conductivity, since the density-specific heat product is a volumetric term, and should not depend on fiber orientation.

Twelve thermocouples were used in each experimental set-up, with two thermocouples at each disk interface with the aluminum cylinders, the heaters, and with the other disks. Only six amplifiers were available on the data acquisition system; therefore, only six thermocouples were actually used for data collection, the remaining ones were installed as a precautionary measure in case one or more of the other thermocouples broke. (Due to the small diameters of these thermocouple wires, they broke very easily.)

Each experiment was repeated at least six times using the same experimental parameters. The experimental parameters for each set of experiments, including fiber stacking angle, stacking order for the disks, temperature, and number of repetitions are shown in Table 4.2.

4.1.6 Fiber Volume Fraction

The fiber volume fractions of disk numbers 5, 6, and 8 (in Table 4.1) were measured by personal at the Composite Materials and Structures Center using an Optimal Numerical Volumetric Analysis (ONVfA) technique developed by Waterbury (1988). In this technique, the density of the samples were first measured by an immersion weighing technique. The samples were then cut through the thickness perpendicular to the fibers and polished. The polished surface was placed under a microscope, and the image was digitized. The fiber volume fraction was calculated from the digitized image, the measured density, and the published densities of the individual fiber and epoxy components, using the ONVfA software developed by Waterbury. These

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Table 4.2 Experimental Parameters for Transient Experiments using Cured Composite Samples.

Exper. No.	Initial[a] Temp. (°C)	Fiber Orientation	Disk Numbers[b]	No. of Repetitions
1.1	29 - 32	$[0°]_{24}$	3,2,1,4	9
1.2	53 - 54	$[0°]_{24}$	3,2,1,4	6
1.3	76 - 78	$[0°]_{24}$	3,2,1,4	6
1.4	101 - 103	$[0°]_{24}$	3,2,1,4	6
1.5	126 - 128	$[0°]_{24}$	3,2,1,4	9
1.6	25 - 29	$[0°]_{24}$	1,4,3,2	6
1.7	49 - 52	$[0°]_{24}$	1,4,3,2	12
1.8	75	$[0°]_{24}$	1,4,3,2	6
1.9	100	$[0°]_{24}$	1,4,3,2	6
1.10	126	$[0°]_{24}$	1,4,3,2	6
1.11	26 - 27	$[0°]_{24}$	5,8,7,6	6
1.12	52 - 53	$[0°]_{24}$	5,8,7,6	6
1.13	75 - 77	$[0°]_{24}$	5,8,7,6	6
1.14	100	$[0°]_{24}$	5,8,7,6	6
1.15	125	$[0°]_{24}$	5,8,7,6	6
1.16	25 - 29	$[0,\pm30,\pm60,90°]_{2(sym)}$	10,11,12,9	12
1.17	52 - 53	$[0,\pm30,\pm60,90°]_{2(sym)}$	10,11,12,9	6
1.18	78	$[0,\pm30,\pm60,90°]_{2(sym)}$	10,11,12,9	6
1.19	25 - 31	$[0,\pm30,\pm60,90°]_{2(sym)}$	11,10,9,12	6
1.20	49 - 53	$[0,\pm30,\pm60,90°]_{2(sym)}$	11,10,9,12	6
1.21	76 - 77	$[0,\pm30,\pm60,90°]_{2(sym)}$	11,10,9,12	6

a. Initial laminate temperatures in experiments.

b. Disk numbers refer to Table 4.1. They are listed in stacking order, from top to bottom.

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results were compared with those obtained using an acid digestion technique, in which the matrix material is dissolved away, so that the remaining fibers can be weighed. The results for both the ONVfA analysis and the acid digestion analysis, including the fiber volume fraction, the void volume fraction, and the density, are shown in Table 4.3.

4.2 Differential Scanning Calorimetry Experiments

Differential scanning calorimetry (DSC) experiments were conducted in order to estimate the kinetic parameters associated with the curing of EPON 828/mPDA epoxy resin. These parameters are those shown in the kinetic models described in Section 3.2. The estimation of the parameters required several isothermal DSC experiments to obtain the heat of reaction at different temperatures, and dynamic or ramped DSC experiments to determine the total heat of reaction. The heat of reaction data was used to calculate the total heat of reaction and the degree of cure, from which the kinetic parameters were estimated as described in Section 3.2.

Samples of neat resin rather than prepreg were used in these experiments, because the required sample size for DSC experiments was small (on the order of 10 mg), and it would have been very difficult to insure consistent sample composition due to the inhomogeneous nature of the prepreg. In using the neat resin, it was assumed that the presence of the fibers had no effect on the cure kinetics. This assumption was justified by the observations of Mijovit and Wang (1989) who found that the presence of carbon fibers had only a very small initial effect on the cure kinetics.

The sample preparation method, the experimental procedures and the experimental parameters for the DSC experiments are presented in the following sections.

4.2.1 Sample Preparation for DSC Experiments

Sample preparation for the DSC experiments involved the preparation of the epoxy resin, the placement of the resin in small special pans, and the closure of the pans with lids. These lids and pans were especially designed for use with the DSC equipment operated in this study.

Table 4.3
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Plate No.[a]	De (k
5	1
6	1
8	1
10[b]	1

a. Plate
b. CNVfA

Table 4.3   Fiber Volume Fractions using Acid Digestion Analysis and Optical Numerical Volumetric Analysis (ONVfA).

Plate No.[a]	Density (kg/m³)	Acid Digestion			ONVfA		
		Fiber Vol. Fr.	Matrix Vol. Fr.	Void Vol. Fr.	Fiber Vol. Fr.	Matrix Vol. Fr.	Void Vol. Fr.
5	1,538.	66.2%	28.6%	5.1%	65.7%	29.3%	5.0%
6	1,531.	64.9%	30.2%	5.0%	66.4%	29.4%	4.2%
8	1,563.	64.7%	32.9%	2.4%	68.5%	28.0%	3.5%
10[b]	1,570.	64.3%	32.4%	3.3%	--	--	--

a. Plate number corresponds to disk number in Table 4.1.
b. ONVfA analysis not appropriate for the quasi-isotropic plates.

The pans and lids designated for use with liquid samples were initially weighed and separated according to weight, and the epoxy was prepared according to the procedures in Section 4.1. Once the epoxy was mixed, several 3cc Becton Dickson single use syringes were filled with the epoxy and placed in a freezer until needed. To prepare a sample for a DSC experiment, approximately 10 mg of epoxy was placed in the center of a tarred pan using the syringe. The weight of the epoxy was then measured and recorded. A lid was placed on the pan, and the pan and the lid were crimped and hermetically sealed together using a crimper for liquid DSC pans (DuPont Instruments, Inc.). Each experiment required a reference pan containing no resin, so a second pan and lid of approximately the same weight as the empty sample pan and lid were also crimped and sealed together. The syringe was placed back in the freezer until further use.

4.2.2 Differential Scanning Calorimeter Operation

A DuPont Instruments Thermal Analyzer System 9900 coupled with a 910 Differential Scanning Calorimeter were used for these experiments. The DuPont 910 Calorimeter is shown in Figure 4.13. The operation procedure consisted of a set up procedure, in which the experimental parameters for each experiment were entered, an initialization procedure, in which the experiment was begun, and after the experiment was completed, a post-processing procedure. These procedures are discussed in the following sections.

4.2.2.1 Differential Scanning Calorimeter Set Up Procedure

The DuPont System 9900 software is menu driven, and the experimental parameters for each experiment were entered using two of these menus: the Sample Info menu and the Select Method menu.

The Select Method menu contains a number of different time-temperature profiles which can be edited to fit the users needs. (The program stores approximately 17 different methods, and each of these methods is designated by a number.) In the Sample
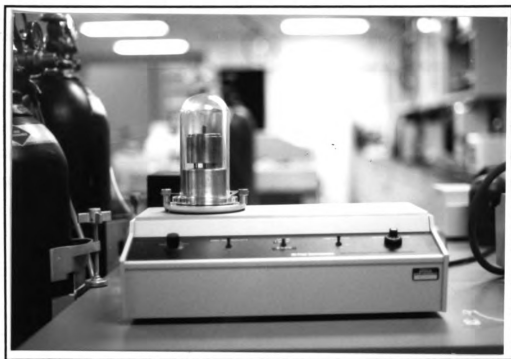
Figure 4.13 DuPont Instruments 910 Differential Scanning Calorimeter.

Info menu, the output data file name is entered, along with the sample weight, the user name, and the method number from the Select Method menu.

In setting up a method in the Select Method menu, several different segments for the time-temperature histories were used. These included INITIAL, ISOTHERMAL, SAMPLING INTERVAL, and RAMP. In the INITIAL segment, the calorimeter cell is heated rapidly to some designated temperature, and it is held at that temperature until prompted by an external trigger by the user to the thermal analysis program; at which time the program proceeds to the next segment. In the ISOTHERMAL segment, the cell is held at its existing temperature for a designated time. The SAMPLING INTERVAL segment is used to set the sampling rate for data collection. In the last segment, RAMP, the cell was heated at a designated rate (i.e., 5°C/min) to a designated temperature.

Using these different segments, the method for the dynamic or ramped temperature experiments was set up as follows:

1. INITIAL: 25°C

2. SAMPLING INTERVAL: 1.0 second

3. ISOTHERMAL: 1 minute

4. RAMP: 5°C/minute to 220°C

In this case, the DSC cell was first initialized at 25°C, and the sampling interval was set to collect data at one second intervals. Upon external trigger to the thermal analysis program, the cell was held at 25°C for one minute, then the temperature was increased linearly at a rate of 5°C/minute until it reached 220°C, at which time the experiment was completed and the cell cooled down to the room temperature.

Similarly, the isothermal experiments were set up using the INITIAL, SAMPLING INTERVAL, and ISOTHERMAL segments to define the time-temperature history.

4.2.2.2 Initialization Procedure for the DuPont 910 Calorimeter

The dynamic experiments were begun after all the necessary parameters had been entered in the Thermal Analysis program. To start the initialization procedure, the bell jar, the cell cover, and the ceramic lid were removed from the DSC cell, and the sample pan and the reference pan were placed on the calorimeter cell as shown in Figures

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4.14a,b. The pans were covered by the ceramic lid, then the cell cover and the bell jar were replaced, and a nitrogen atmosphere was induced into the bell jar at a rate of 50 cc/minute. The data acquisition and controlled heating cycle was then initiated through the thermal analysis program.

The isothermal experiments were initiated differently. Since it was desired to achieve isothermal conditions throughout these experiments, it was important to minimize the heating time for the sample. To do this, the calorimeter cell was first preheated to the desired temperature using the INITIAL segment, and the rate was set for the nitrogen atmosphere into the bell jar. The ISOTHERMAL segment was then started, and the bell jar, the cell cover, and the ceramic lid were removed. The reference and samples pans were then placed in the calorimeter cell, and the jar, cover, and lid were replaced as quickly as possible. The time required to complete these maneuvers after the ISOTHERMAL segment was started was approximately 30 to 40 seconds.

4.2.2.3 Post-Processing Procedure

After the completion of each experiment, several post-processing programs associated with the Thermal Analysis System were utilized.

In each repetition of the dynamic DSC experiment, the area under the heat of reaction rate cure was integrated, and the total area under each curve or the total heat of reaction for that experiment, was determined using the Thermal Analysis software. The heat of reaction rate data and the integrated data (the cumulative heat of reaction) were then plotted using the Thermal Analysis plotting subroutines. The resulting plot for one repetition of the dynamic DSC experiment is shown in Figure 4.15.

In each of the isothermal experiments, the associated baseline was subtracted off the heat of reaction rate curve, and the results were plotted using the plotting subroutine. A baseline consists of the heat of reaction data for a sample after it has been fully cured, assuming the same curing method; it serves as a reference line for the heat of reaction rate data of the samples during curing. After the baseline was subtracted off, the modified heat of reaction rate data was then transferred to a floppy disk in ASC format for later processing.

Figure 4.14a DuPont Instruments 910 Differential Scanning Calorimeter Cell (left), Showing Bell Jar (right), Cell Cover (center), and Ceramic Lid (on cell)

Figure 4.14b Close-up View of Sample Pan (right) and Reference Pan (left) in Calorimeter Cell Shown Above.
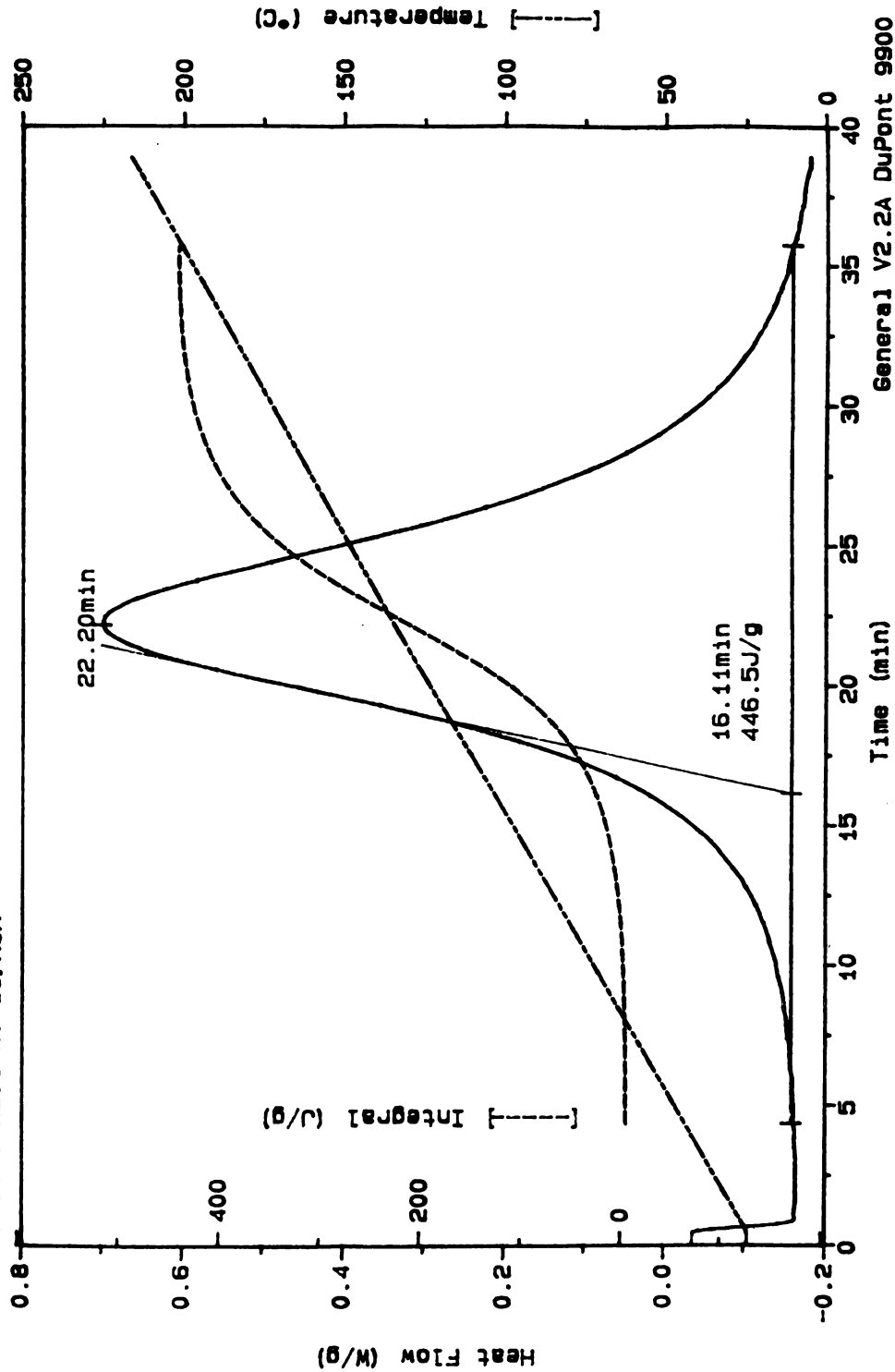
Figure 4.15 Heat of Reaction Data from One Repetition of the Dynamic DSC Experiment using DuPont Thermal Analysis Plotting Subroutines

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4.2.3 Experimental Parameters

Four different sets of isothermal experiments and one set of dynamic experiments were conducted using the DuPont Thermal Analyzer System 9900. The dynamic experiments were conducted using the segment methods discussed in Section 4.2.2. These experiments were repeated eight times, with each experiment running for about 40 minutes.

The four temperatures for the isothermal experiments were chosen using the procedure described by Sichnia (DuPont Applications Brief No. TA-93). Using this procedure, the isothermal temperatures were chosen from an interval defined between 10°C below the onset of cure and a point midway to the peak maximum of a thermoset heated at a rate of 5°C/min. Since the dynamic experiments followed this heating rate, the temperatures were selected using these thermosets. Sichnia recommended that the selected isothermal temperatures be 5°C to 10°C apart. Figure 4.16 shows a heat of reaction curve from one of the dynamic DSC experiments with the interval for the isothermal temperatures indicated. Based on this interval, the isothermal experiments were conducted at 60°C, 70°C, 100°C, and 110°C, with three repetitions at each temperature.

Preliminary experiments were run to establish the required curing time at each temperature. The resulting time-temperature segments used for each set of isothermal experiments are given below.

                    60°C: INITIAL: 60°C

                           SAMPLING RATE: 2 seconds

                           ISOTHERMAL: 300 minutes

                    70°C: INITIAL: 70°C

                           SAMPLING RATE: 2 seconds

                           ISOTHERMAL: 240 minutes

                    100°C:INITIAL: 100°C

                           SAMPLING RATE: 1 second

                           ISOTHERMAL: 90 minutes

                    110°C:INITIAL: 110°C

DSC

Sample: THR25_220.01
Size: 19.0000 mg
Method: 25 C-220 C 5 I C/MIN
Comment: 25°C-220C AT 5C/MIN

Sample: THR25_220.01
Size: 19.0000 mg
Method: 25 C-220 C 5 I C/MIN
Comment: 25°C-220C AT 5C/MIN

DSC

File: A:THREPS.02
Operator: SCOTT
Run Date: 05/09/89   14:02

Heat Flow (W/g)

Temperature (°C)

Optimal Interval

General V2.2A DuPont 9900
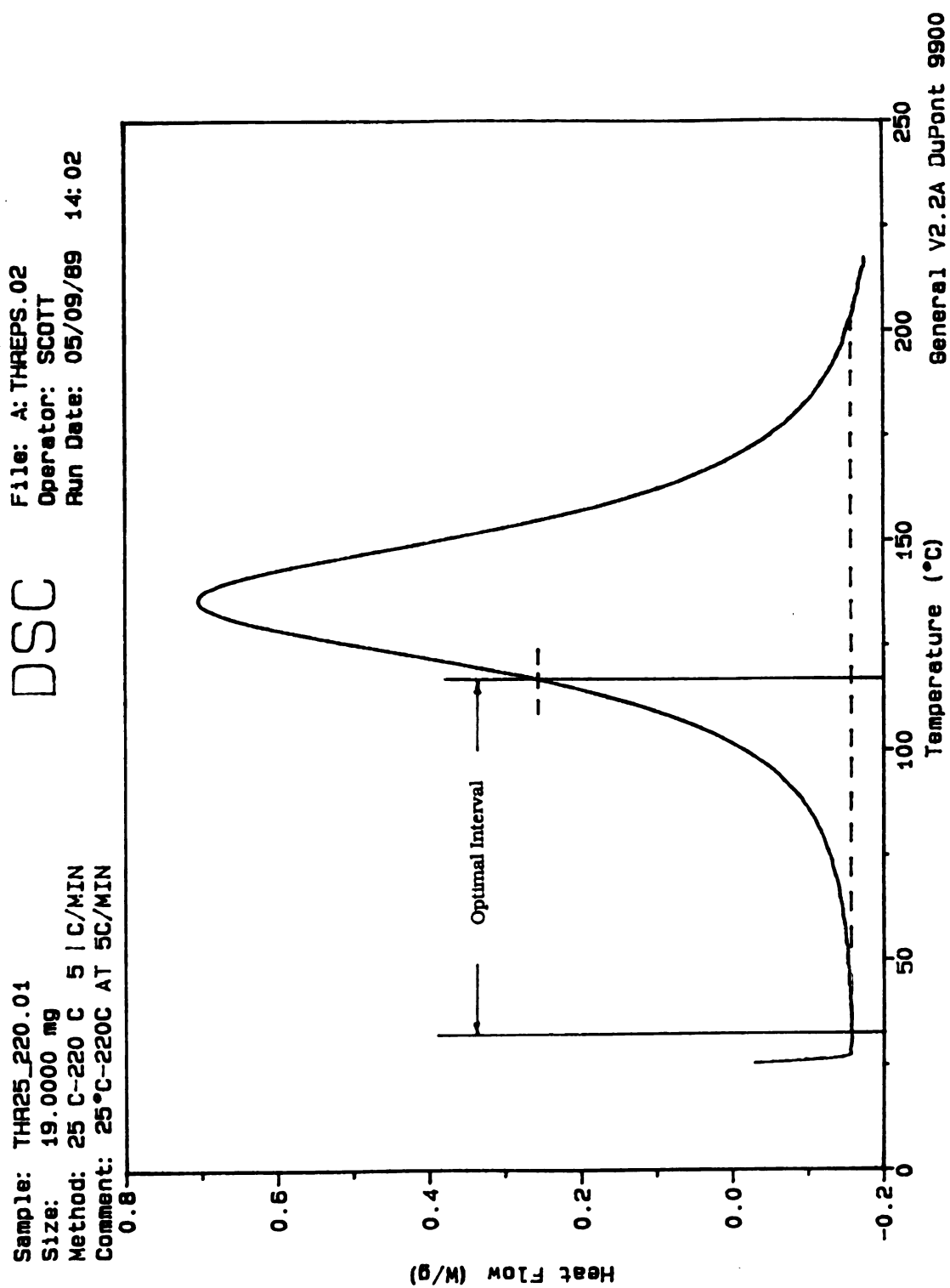
Figure 4.16 Determination of Temperatures for Isothermal DSC Experiments from a Dynamic DSC Experiment

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SAMPLING RATE: 1 second

ISOTHERMAL: 60 minutes

Each of the above isothermal segments was also repeated once using a previously cured sample pan to establish a baseline for each temperature regime.

A summary of the DSC experiments, including the time, temperature, and number of repetitions is shown in Table 4.4.

4.3 Transient Temperature Measurements during Curing

The transient temperature experiments discussed in this section were similar to those described in Section 4.1 for the transient temperature experiments using cured composite samples; however, in these experiments, the temperature measurements were taken during the curing process; therefore, the prepreg laminate was instrumented with thermocouples and heaters during the stacking process. Two experiments were conducted using the procedures described in this section. In the first experiment, the data acquisition procedure was similar to that described in Section 4.1.3, except that a VAXstationII/GPX microcomputer was used instead of the Plessey system. A new data acquisition procedure was developed for the second experiment which included new amplifiers and a new computer controlled power supply for the heaters. These two experiments will be referred to as Exp. 3.1 and Exp. 3.2 in subsequent chapters. Finally, one additional experiment (Exp. 3.3) was conducted using the cured samples from Exp 3.2 under similar experimental conditions.

In each experiment, the heaters were activated at regular intervals throughout the curing process. In the analysis, procedure, these intervals were considered separately, so that each curing experiment could be considered as a combination of 15 to 20 shorter experiments. The procedures used for these experiments are given in the following sub-sections.

Table 4

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Table 4.4 Experimental Parameters for Differential Scanning Calorimetry Experiments.

Exper. No.	Experiment Type	Temperature (°C) (Heating Rate)[a]	Time (min)	No. of Repetitions[b]
2.1	Dynamic	25°C-220°C (5°C/min)	39	8
2.2	Isothermal	60°C	300	3
2.3	Isothermal	70°C	240	3
2.4	Isothermal	100°C	90	3
2.5	Isothermal	110°C	60	3

a. For dynamic experiments only.
b. Does not include experiments to establish baselines.

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<u>4.3.1 Sample Preparation</u>

Prepregs, composed of EPON 828/mDPA epoxy and continuous AS4 carbon fibers, were also used in these experiments. The epoxy was prepared according to the procedures in Section 4.1.1.1, and the prepregs were prepared following the procedures outlined in Section 4.1.1.2. The prepreg plies were stacked with thermocouples and heaters embedded between the plies; these thermocouples were prepared according to the procedure given in Section 4.1.2.1. The preparation procedure for the the heaters and the stacking process are discussed in the following sub-sections.

4.3.1.1 Heater Preparation

Thin, flat, resistance heaters were used to supply the heat flux boundary condition in the transient experiments. Two 7.6 ohm Thermofoil^R heaters (Minco Products, Inc.) were laid on top of each other so that the heating elements were not overlapping and held in place using a very thin layer of the Silicon Heat Sink Compound (Dow Corning Corp.). The heated surface of the heaters measured 12.4 cm by 9.8 cm. A sheet of aluminum foil was cut and adhered to each side of the heaters using the silicon compound to protect the heaters from the epoxy resin and to insure a uniform heat distribution.

4.3.1.2 Stacking Procedure

The prepreg was instrumented with the thermocouples and the resistance heaters during the stacking procedure. Forty-four plies were cut from each prepared prepreg, and then they were stacked with the fibers parallel to each other ($[0°]_{44}$) and instrumented symmetrically with the thermocouples and the heaters. The instrumented prepreg laminate was set between porous Teflon^R cloths, bleeder cloths, and flat, smooth aluminum plates covered with release ply, and then the entire assembly was placed in a vacuum bag for curing. This procedure is very similar to the procedure described in Section 4.1.1.3, with some important differences, such as the instrumentation of the laminate with the thermocouples during the stacking process, and the

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inclusion of the bleeder and Teflon^R cloths on both sides of the laminate. An outline of this process follows.

1. Two 15.2 cm by 17.8 cm pieces were cut from the porous Teflon^R cloth, the bleeder cloth, and the release ply plastic. In addition, a small piece of thick bleeder cloth (approximately 8 cm by 10 cm) and piece of vacuum bag material at least 40 cm by 66 cm were cut.

2. The prepreg was taken out of the freezer, and allowed to cool just enough to become pliable (approximately 5 minutes), and dry ice was obtained and chopped into small chunks.

3. The prepreg was spread out on a sheet of foil, and a piece of poster board was placed under the section to be cut. Using a carpenters square as a guide, forty-four 10.2 cm by 12.7 cm plies were cut from the prepreg using a utility knife with a sharp blade.

4. One piece of the release ply was adhered to a smooth 23 cm by 23 cm aluminum plate, using small amounts of Tacky Tape^R at the corners.

5. Several prepreg plies were laid out on the foil, and the remaining pieces were placed back in the freezer until needed. Using thermal gloves, the dry ice was spread over the pieces of prepreg, and one of the release plies on each prepreg ply was removed, taking care not to peel off any fibers with the plastic.

6. After any frost which had accumulated on the exposed surface had evaporated off, two prepreg plies were stacked together with the fibers parallel to each other. This process was repeated with the other plies, except that some plies were instrumented with thermocouples, and a resistance heater was placed at the mid-plane of the plies (step 7.).

7. The plies were instrumented with thermocouples by placing the thermocouple junction at the center of the exposed prepreg surface, with the exposed portion of the wires oriented perpendicular to the fibers. A second ply was stacked as described above, taking care to keep the thermocouple in place. The resistance heater was placed in between the middle two plies. A roller was used in an effort to remove air trapped between the plies or between the prepreg and the heater.

8. Once the prepreg laminate had been stacked and instrumented, one of the last two release plies was removed, and a piece of porous Teflon^R cloth was centered on the exposed surface. The sample was then placed on top of one of the bleeder cloths placed on the aluminum plate covered with release ply.

9. Cork tape was used to as a dam around the sample. The dam was built up until it was level to the sample thickness; special care was taken not to disturb the thermocouple wires and the heater connectors.

10. The last release ply was removed from the sample, and the exposed surface was covered with the second pieces of porous Teflon^R and bleeder cloth. Finally, the aluminum plate covered with release ply was placed on top of the bleeder cloth. A stacked composite laminate, with the porous Teflon^R and bleeders cloths cut away to expose the thermocouples at the surface, is shown in Figure 4.17. (This photograph was taken after curing.)

11. The entire assembly was placed on one half of the vacuum bag material and the other half of the sheet was folded over the assembly. Tacky Tape^R was used to seal the bag, and a short rubber hose (approximately 12 cm long) was placed at one end. The remaining piece of thick bleeder cloth was placed over the mouth of the tube and held in place with Tacky Tape^R. The assembly was checked visibly for leaks, and extra tape was added where needed, especially around the rubber tube. A stacked and instrumented laminate, sealed in a vacuum bag is shown in Figure 4.18.

12. The vacuum bag with sample enclosed was placed in the freezer until ready for curing.

4.3.2 Experimental Set-up

The curing process for thermoset epoxy composites requires both elevated temperatures and applied pressure. The required temperature regime was obtained by curing the stacked prepreg laminate in a laboratory oven (Matheson Scientific), and a mechanical press was designed and built to fulfill the pressure requirements. The required pressure for the type of epoxy used is 689 kPa (100 psi), and the composite
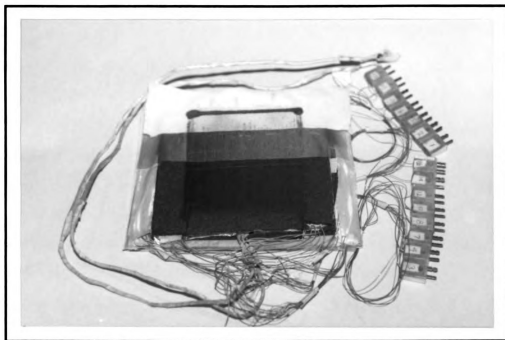
Figure 4.17 Stacked Composite Prepreg, Instrumented with Thermocouples and Heaters. (Photograph taken after curing.)
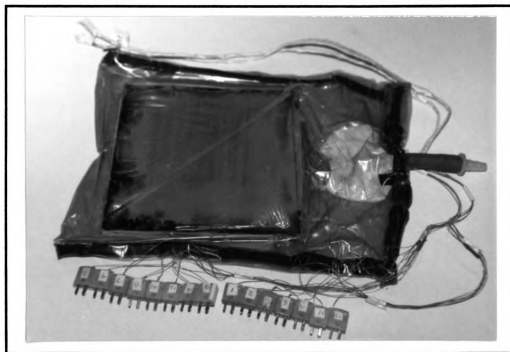
Figure 4.18 Stacked and Instrumented Composite Prepreg Sealed in a Vacuum Bag.

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samples were approximately 12.7 cm by 10.2 cm (see Section 4.3.3), resulting in a required load on the sample of 890 N.

The press was designed using two 28 cm by 28 cm by 1.2 cm thick steel plates and eight 5 cm compression springs with springs constants of 175 N/cm. The design called for eight 1.3 cm holes to be drilled in each plate, four at each corner, and four at the midplane of each edge, at a location 1.9 cm from each edge. The springs were to be held in place at these locations using 1.3 cm by 12.7 cm long bolts with the appropriate nuts. The press was designed such that the stacked prepreg laminate sealed in the vacuum bag lay between the plates, and the bolts fastened the plates together with the springs on top of the plates. Pressure was applied through the deflection of each spring 0.75 cm, which resulted in a total force from the eight springs of 890 N. (The weight of the upper plate was subtracted from the required load in determining the required deflection for each spring.) A photograph of the press design with the composite laminate in place is shown in Figure 4.19. The press was machined at the MSU College of Engineering Machinery Shop.

It should be noted that preferably the autoclave or the hydraulic press discussed in Section 4.1.1.4 would have also been used in this consolidation process. These devices are preferable because they allow for uniform pressure and temperature on both sides of the composite throughout the curing process. Neither the autoclave or the hydraulic press could be used, however, because the data aquisition system and this equipment were situated in different locations, and none of these could be moved easily.

4.3.3 Data Acquisition and Controlled Heat Flux

The VAXlab system (Digital Equipment Corporation) was used to record temperature data during both the transient temperature experiments. In the first experiment, one analog-to-digital (A/D) converter was utilized, and in the second experiment, two A/D converters and one digital-to-analog (D/A) converter were incorporated. The A/D converters were used to record temperature data from the thermocouples in the composite sample, and in the second experiment, the D/A converter was used to control a
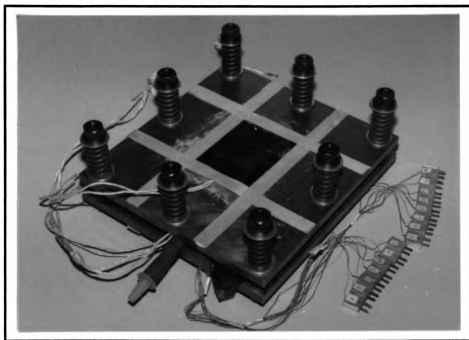
Figure 4.19 Mechanical Press with Composite Laminate in Place.

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power supply which supplied the heat flux for the resistance heater. The thermocouples produced a signal on the order of millivolts, and amplifiers were used to amplify the signal for the A/D input. New amplifiers were used in the second experiment, while the Data Translation amplifiers (Section 4.1.3.2) were used in the first experiment. Two different computer programs were employed for these experiments. In the first case, the programs used on the Plessey system (Section 4.1.3.3) were modified to run using the VAXlab system subroutines. A new program was developed for the second experiment, using both the A/D and D/A converters.

The details of the data acquisition systems used for the two experiments are given in the following sub-sections. Schematics of the data acquisition systems for the two experiments are given in Figures 4.20 and 4.21.

4.3.3.1 The VAXlab Data Acquisition Hardware

The VAXlab system was run on a VAXstationII/GPX microcomputer (Digital Equipment Corporation). The system hardware included a KWV11-C real time clock board and two AXV11-C combination boards with one A/D converter and two D/A converters each. Each A/D converter was set for a maximum of eight channels. The AXV11-C boards were equipped to run using synchronous (sequential) or asynchronous (continuous) input/output (I/O), however the asynchronous I/O was limited to using only the A/D or the D/A, but not both. Therefore, the asynchronous I/O was used in in the first experiment, and the synchronous I/O was used in the second experiment which included a controlled power supply. The KWV11-C is a clock module which can be used to trigger the AXV11-C devices. In the second experiment, the clock was attached to both boards so that there was a total of sixteen available A/D channels. The signal range for the A/D converters was set from 0 to 10 volts, and the range for the D/A converter used in the second experiment was set from -10 to 10 volts.
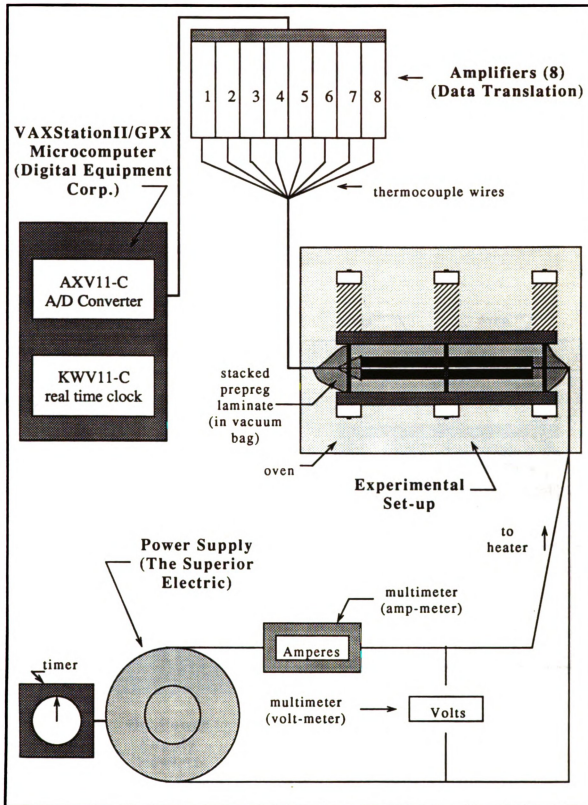
Figure 4.20 Schematic of Data Acquisition for First Transient Experiment during Curing.
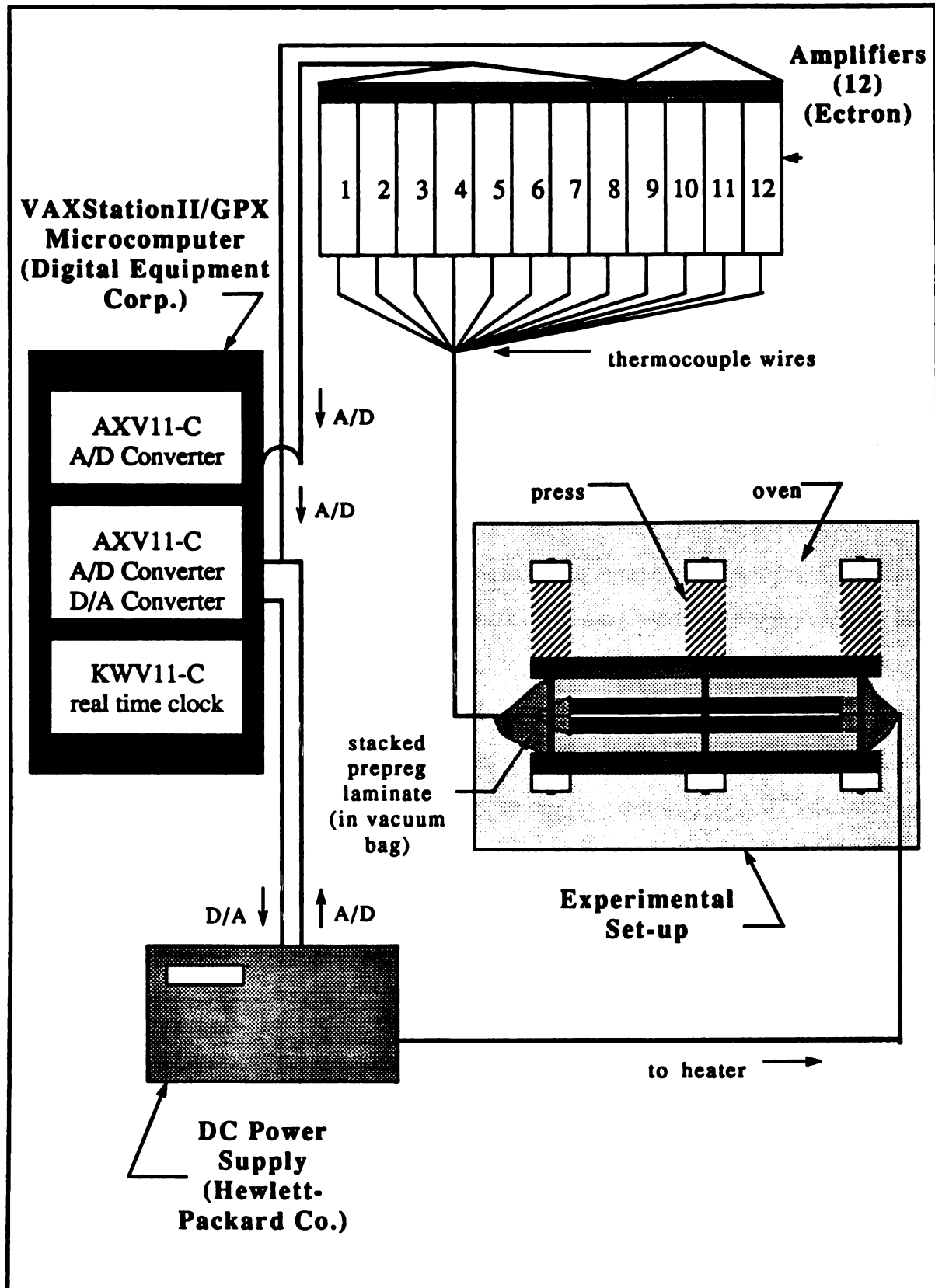
Figure 4.21 Schematic of Data Acquisition for Second Transient
Experiment during Curing.

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4.3.3.2 Signal Amplification

Since the signal from the thermocouples was on the order of millivolts and the range of the A/D converters was from 0 to 10 volts, amplifiers were used to amplify the signals.

The eight Data Translation amplifiers discussed in Section 4.1.3.2 were also used for the first experiment on the composite samples during curing, and twelve new Model 687 DC Amplifiers (Ectron Corporation) were used in the second experiment. These Model 687 amplifiers were equipped with set gains of 10, 20, 50, 100, 200, 500, and 1000, with a vernier adjustment to obtain values between the set points, and the frequency response of these amplifiers was on the order of 3 kHz. A gain of 1000 was used in this case. The remainder of this sub-section focuses on the Model 687 amplifiers.

Two optional accessories, Model 683, Universal Thermocouple Adaptor (UTA), and Model 684, Ambient Temperature Compensator (ATC), were installed on each Model 687 amplifier for operation with thermocouple inputs. The Universal Thermocouple Adaptors were attached to the input connector at the rear of each amplifier, which served as the reference junctions for the thermocouples. The ATC is a card which was attached to the amplifier board and operated in conjunction with the UTA to simulate an ice point reference junction for the particular type of thermocouple used, which was in this case Type E, chromel-constantan.

Prior to use, the gains and zeros of the amplifiers were checked according to the instruction manual for the amplifiers (Ectron Corporation, 1982). To check the actual gain of each amplifier, a power supply with set voltage outputs was connected to each amplifier, bypassing the UTA. Then, one and ten millivolt signals were sent to the amplifier, and the output signals were recorded with the set gain at 1000. From these readings, the fractional differences between the set gain and the actual gain were determined.

The amplifiers were zeroed with the UTA switched off. There are two zero controls on the amplifiers: a referred to input (RTI) potentiometer and a referred to output (RTO) potentiometer. To zero the amplifiers, a jumper was first connected across the signal

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input terminals, then the gain was adjusted to 10, and any offset (from zero) was removed using the RTO potentiometer. Then the gain was set to 1000, and any offset was removed using the RTI. This process was repeated until a zero reading was obtained from both RTO and RTI potentiometers.

The actual reference junction temperature was also measured and adjusted. After adjusting the RTO and RTI potentiometers, the UTA was turned on, and thermocouples were connected to the amplifiers. The junctions of the thermocouples were placed in a 0°C electronic ice bath (Omega, Inc.), and the output signals from the amplifiers were adjusted to read 0.0 mvolts using the potentiometer on the UTA card.

4.3.3.3 Controlled Heat Flux

The same power supply apparatus described in Section 4.1.3.4 was also used in the first transient experiment during curing. The timer was operated manually at regular intervals throughout the curing cycle to provide the required heat flux to the heaters.

In the second experiment, the input voltage to the resistance heaters were controlled using a DC power supply (Model 6024A, DC Power Supply, Hewlett-Packard Co.). The Model 6024A is an autoranging 200 W power supply, with an operating range of 0 to 60 volts and 0 to 10 amps, and with remote programming capabilities. The power supply was operated in a constant voltage, voltage control mode, where an input voltage source from 0 to 5 volts produced a proportional output voltage from zero to full scale. The actual output voltage of the power was measured remotely. The input voltage source was obtained from the VaxStationII/GPX D/A converter, and the output voltage was read by one of the A/D converters. Since the voltage ranges for both the A/D and the D/A on the VaxStationII/GPX were set at 0 to 10 volts, the input voltage source to the power supply was scaled to 0 to 5 volts using a 2:1 divider, and the output voltage was scaled from 0 to 60 volts to 0 to 10 volts using a 6:1 divider.

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4.3.3.4 Data Acquisition Program

The data acquisition programs, *DATACQ* and *DATFIT* (Osman, 1987), were combined and modified to run on the VaxLab system for the first experiment during curing. This new program, *DATAAQ*, utilized the Vaxlab LabStar I/O Routines (LIO) (Digital Equipment Corporation, 1986) to read thermocouple data using one of the A/D converters. The operating mode of this program was similar to that described for *DATACQ* and *DATFIT* in Section 4.1.3.3. The remainder of this section is devoted to the discussion of a new data acquisition program, *DATA_DA_AD* (Appendix B), which was used in the second curing experiment.

DATA_DA_AD was written for the VaxStationII/GPX to read from the thermocouples and the power supply using the two AXV11-C A/D converters, while writing to the power supply using an D/A converter on one of the AXV11-C devices. These operations required the use of the LIO routines. The program converts the binary voltage readings from the thermocouples to temperature using the LabStar Signal-Processing Routines (LSP) (Digital Equipment Corporation, 1986), and it converts the binary voltage readings from the power supply to heat flux. The program also sets up a data file for use in the parameter estimation program, *PROP1D_CURE*. A schematic of the program and its subroutines is shown in Figure 4.22, and a detailed description of the program is now presented.

The parameters required for data acquisition are first entered using the subroutines *SETUP_DATA*, *SETUP_POWER*, and *SETUP_AMP*. In the first subroutine, *SETUP_DATA*, the user enters the sampling interval, the total number of A/D channels (maximum of twelve), and the total number of data points points for each channel. In addition, the program allows the user to average data within each sampling interval, so that the number of data points to be averaged over each sampling interval is also entered. In the second subroutine, *SETUP_POWER*, the parameters for the controlled heat flux are entered. These values include the surface heated area of the sample in the transient experiments, the resistance of the heater, and the input voltage data for the power supply, namely, the times at which the power supply is activated, and the desired voltage input corresponding to that time. The D/A is set up in such a way that
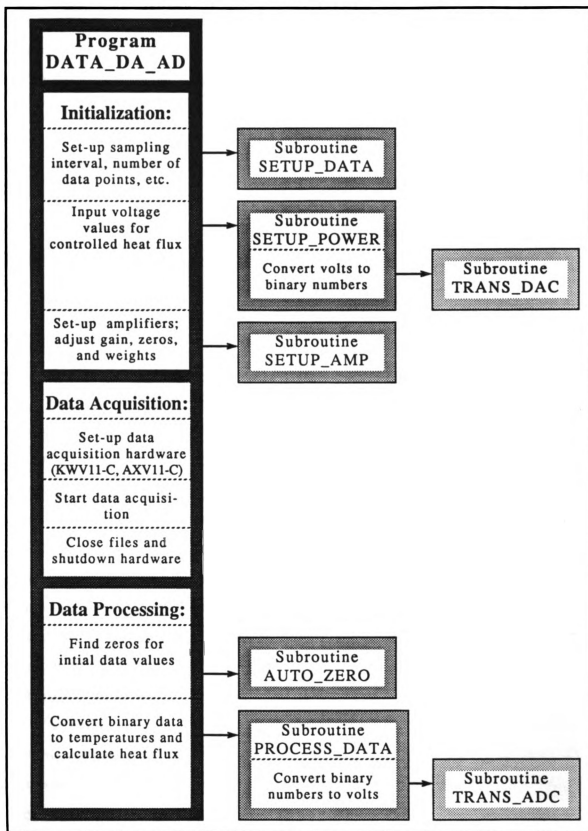
Figure 4.22 Schematic of Data Acquisition Program *DATA_DA_AD*.

once it was activated, it continued to send the same signal until the signal was changed. These data are converted to binary format in subroutine TRANS_DAC, where the input 0 to 10 volts are scaled to approximately 0 to 2048 in binary format.

Finally, the $0°C$ reference junctions, the gains and the weights of the amplifiers can be adjusted in subroutine SETUP_AMP. The $0°C$ reference junctions may be adjusted by the user, or the program will calculate the 'zeros' by averaging the first few data points over a time in which no heat flux is applied, assuming the conditions are isothermal. The gains of the amplifiers can also be adjusted, and a weighting factor is assigned to each amplifier. These values are either set to one or to zero, for the case of a 'bad' amplifier or a broken thermocouple.

Once the initial set up procedure has been completed, the program begins the data acquisition hardware setup, which utilizes the LIO routines. First the devices are attached, including the KWV11-C clock, and the two AXV11-C boards (AXV11-Ca and AXV11-Cb). The clock is then set up to read data at the desired rate, and both AXV11-C devices are set up to read the desired number of channels from the A/D converters. The AXV11-Ca device is set up to sweep through all channels on each clock trigger, while the AXV11-Cb device is set up to trigger on the 'READ' statement of the AXV11-Ca device. The AXV11-Cb is also set to write to the power supply using the D/A converter.

The clock is started by a trigger from the user, and data is read from the A/D converters and written to the D/A converters synchronously. The data is immediately written to a file after it is read, in case of unexpected program interruption. Once the desired number of data points have been read, the program begins the shut down procedure, in which a terminating zero voltage is sent to the power supply, and the clock is stopped, and the devices are detached.

The analysis portion of the program then begins. If indicated, the $0°C$ reference junctions are calculated in subroutine AUTO_ZERO. Here the binary reading from the thermocouples are averaged over the first few time step, and the 'zeros' for each channel are calculated from

$$z_i = (B_i^{avg} - B_i^{avg}g_i)/n_t$$

where z_i is the 'zero' adjustment for the ith channel, B^{avg} is the average of the binary data over all the channels and over n_t time steps, B_i^{avg} is the same average, but just for the ith channel, and g_i is the gain for the ith channel.

The subroutine *PROCESS_DATA* is used in the rest of the analysis. The data are first converted to voltages using *TRANS_ADC* (0 to 4095 - 0 to 10 volts), and the data from the power supply are adjusted to the actual range of the power supply (0 to 60 volts). The data readings from the thermocouples are then adjusted to account for the gains and the 0°C reference junctions as follows:

$$V_i^a = V_i g_i + z_i$$

where V_i^a is the adjusted voltage for the ith channel and V_i is the unadjusted voltage. These values are converted to °C using one of the signal processing subroutines, *LSP$THERMOCOUPLE_E*, in the Vax LabStar system, which is specifically for Type E, chromel-constantan, thermocouples. The heat flux associated with the resistance heaters is calculated from the heated area, the resistance of heater, and the voltage measurements. Finally, the time, heat flux, and thermocouple readings in °C are written to a file for use in the parameter estimation program, *PROP1D_CURE*.

4.3.4 Experimental Procedure for Transient Temperature Measurements during Curing

The procedures for the two experiments to measure temperature in the carbon/epoxy composite during curing were similar, except that some of the procedures used in the first experiment were modified in the second experiment due to the purchase of new amplifiers and a new powers supply. In both experiments, the stacked prepreg laminate (Section 4.3.1.2) was cured in the press as described in Section 4.3.2, using the standard cure cycle recommended for this type of composite (Rich, 1987). This cycle included a heating up period from room temperature to 75°C, a two hour isothermal period at 75°C, a second heating period to 125°C, and a two hour isothermal period at 125°C. (This is the same cure cycle used for the disks prepared for the transient experiments using cured composite samples, described in Section 4.1.1.) The

heaters embedded in the laminate were activated at regular intervals throughout the the curing cycle. The data acquisition programs were set up to record temperature data continuously throughout the entire cure cycle.

At the beginning of each experiment, the laboratory oven (Section 4.3.2) was first preheated to 75°C, and the appropriate data acquisition program for each experiment was set up. The prepreg laminate, sealed in a vacuum bag, was then taken from the freezer in the Composite Materials and Structures Center and set out at room temperature for about five minutes. A valve was attached to the rubber hose on the vacuum bag, and then it was connected to a vacuum pump. Pressure was reduced in the bag to -99 kPa for ten minutes. At this time the valve was closed, and the vacuum bag, including the short hose and valve, was disconnected from the vacuum pump and transported to Rm. A-32, Research Complex / Engineering as quickly as possible. The vacuum bag was placed in the press, then the press was assembled, and pressure was applied to the laminate through the depression of the springs on the press. Due to the large mass of the press, extra heaters were attached to the top and bottom extremities of the press to reduce the heating time required to heat the press from 25°C to 75°C and from 75°C to 125°C. (These heaters were disconnected during the short heating intervals throughout the isothermal periods.)

The press was then placed in the preheated oven, and the thermocouples were connected to the extension thermocouple cables, and the heaters were connected in parallel to the power supply as quickly as possible. The oven door was closed, and the data acquisition program was started, along with a separate stop watch.

In the first experiment, the same power supply discussed in Section 4.1.3.4 was used. The power supply was disconnected from the timer during the initial heat up period in the curing cycle and during the heat up period from 75°C to 125°C. During these periods, power was continuously supplied to the internal heaters in the stacked laminate and to the heaters fixed on the surface of the press in order to reduce the time required to heat the sample and the press. At the end of the first heat up period, when the laminate temperature was close to 75°C, the power supply was disconnected from the heaters on the press and reconnected to the timer. Using the stop watch to record

events with respect to overall experimental time. The heaters embedded in the laminate were activated at regular intervals using the timer, throughout the isothermal curing period at 75°C. At the end of the first isothermal period, the timer was disconnected, and the oven temperature was set at 125°C. The heaters on the press were reconnected, and power was supplied to the heaters in the same manner as in the first heating up period. Once the laminate was close to 125°C, the heaters on the press were disconnected, and the timer was reconnected, and the heater embedded in the laminate was activated at regular intervals as before. The output temperature responses resulting from the imposed heat fluxes were recorded continuously throughout the whole experiment using the data acquisition program, *DATAAQ*.

In the second experiment, the power supply was computer controlled so that the complete history, including the heating up periods and heating intervals during the isothermal portions of the cure cycle, for the power supply output was entered through the data acquisition program at the beginning of the experiment. The stop watch was activated at the time the sample was placed in the oven, in case of an unplanned interruption in the data acquisition program, and the external heaters on the press were connected during the initial heating up period to 75°C. At the end of the first isothermal period, the oven temperature was increased to 125°C, and the external heaters on the press were once again connected during the heating up period from 75°C to 125°C. The output responses from the thermocouples and from the power supply were read continuously using the data aquisition program, *DATA_DA_AD*.

In both experiments, after the curing cycle was completed, the oven was turned off, and the data processing portions of the data acquisition programs were completed. Once the cured samples were completely cooled, they were cut apart at the thermocouple junctions, perpendicular to the thermocouples, using a diamond circular saw, and then the exact thermocouple locations at the cut surfaces were measured.

4.3.5 Experimental Parameters

The experimental parameters in the transient temperature experiments on the carbon/epoxy composite materials during curing included the curing cycle, the data

sampling interval, the heating interval for the embedded heaters during the isothermal curing periods, the frequency of the heating intervals, the magnitude of the heat flux, fiber orientation with respect to the heat flux, the number of plies in the laminate, and the position and number of thermocouples.

In both experiments, the recommended curing cycle discussed previously was followed. Due to the mass of the press, the heating up periods took much longer than the usual 20 minutes recommended. Therefore, the isothermal periods were shortened slightly to account for the longer heat up time. The fibers were oriented perpendicular to the heat flux, and forty-four plies were used in both experiments, resulting in two cured laminate plates approximately 4 mm thick for each experiment. (There was one plate on either side of the heater.) Due to the type of press used in the experiments, it was felt that an attempt to cure a thicker sample might result in an increased number of voids.

In Exp. 3.2, which was the first experiment, the data sampling interval was limited to six seconds, due the data acquisition program used. The heating interval was set at forty seconds, consistent with that used in the experiments with the cured composite samples. The heating intervals were repeated every ten minutes with the exception of the first two which were repeated at six minute intervals. This resulted in a total of fifteen heating intervals throughout the curing cycle. The output power from the power supply was adjusted to approximately 50 watts for the first half of the heating intervals and 100 watts for the second half. A total of twelve thermocouples were embedded in the laminate during the stacking process, but only four of the data translation amplifiers were working at the time of the experiment; therefore, two thermocouples on either side of the heater, and the two thermocouples next to the top and bottom plates of the press were used for data acquisition, as shown in Figure 4.23.

In the second experiment, the data acquisition program was adjusted so that data was recorded every second. The duration of the heating intervals was determined using the optimal experimental criterion discussed in Section 3.4. First, the dimensional heating time was determined from eq. (3.24h), using the optimal dimensionless heating time of 2 based on the assumption that the dimensionless heat generation term in eq.
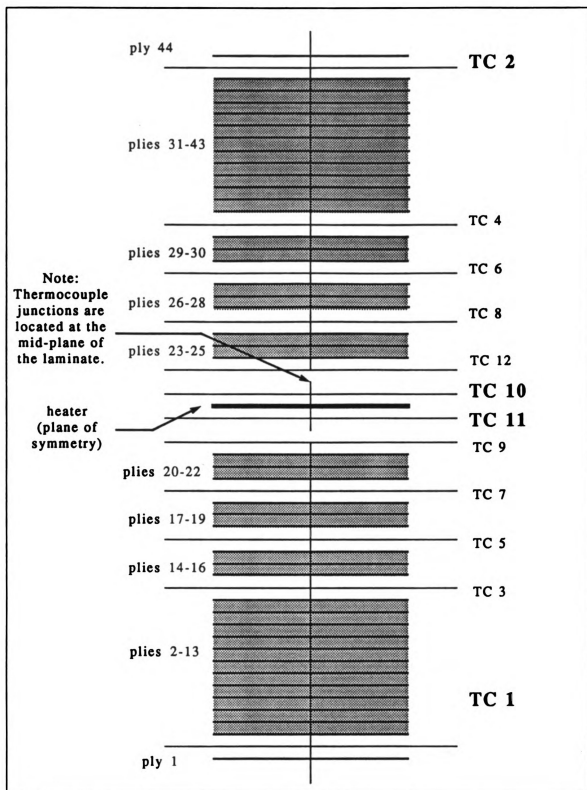
Figure 4.23 Thermocouple (TC) Locations in Prepreg Laminate for the First Transient Experiment during Curing. Plies are Numbered from Bottom to Top, and the Thermocouples used in Data Acquisition are Numbers 1, 2, 10, and 11 (shown in boldface type).

(3.24f), g^*, was equal to 1, a thermal diffusivity value determined from the cured composite at 100°C, and the thickness was chosen as a fixed value equal to the maximum of the values shown in Table 4.1. This resulted in an optimum heating interval of approximately 135 seconds. (Alternatively, one could also optimize the thickness of the sample for a given heating rate.) In order to reach steady state conditions after each heating interval, 500 seconds were required between each interval.

The heat flux used in this experiment was determined from eq. (3.24e), with a maximum temperature rise of 5°C. The dimensionless temperature, T^*, in eq. (3.24e) was determined from eq. (3.25a) using the optimum heat time, t_i^*, and g^* equal to 0.1. This resulted in a value of T^* equal to 1.045, and the required heat flux was calculated to be approximately 800 W/m^2 . The results of the DSC experiments (Section 4.2) were used to justify the assumption of g^* equal to 0.1. The heat generation term in eq. (3.19a) is proportional to the heat of reaction rate ($H_t d\alpha/dt$), and the heat of reaction rate was determined from the maximum heat of reaction rate data from the DSC experiments conducted at 70°C. The maximum heat of reaction was approximately 50 W/kg at this temperature. Using this value as the heat of reaction rate, and the density values shown in Table 4.3, the calculated dimensionless heat generation term was approximately 0.4, which is on the order of 0.1, supporting the assumption of g^* equal to 0.1. (Note that there was very little difference (<6%) between the optimal heating times reported Section 3.4.2 for $g^* = 0.1$ and $g^* = 1.0$.)

A total of sixteen thermocouples were embedded in the laminate during stacking, but since there were only twelve Ectron amplifiers, only twelve thermocouples were actually used for data acquisition. The locations of these thermocouples are shown in Figure 4.24.

One additional experiment was conducted using the cured samples from Exp. 3.2 under similar experimental conditions; however, the heat flux during the heating intervals was increased from 800 W/m^2 to 1500 W/m^2 . This experiment is referred to as Exp. 3.3 in Chapter 5. The purpose of this experiment was to provide a means of evaluating the experimental procedures using during the curing experiments, since
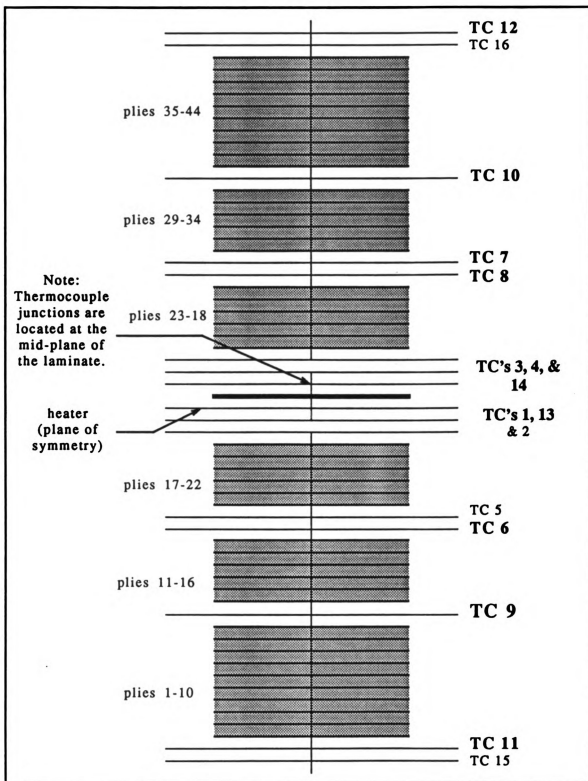
Figure 4.24 Thermocouple (TC) Locations in Prepreg Laminate for the Second Transient Experiment during Curing. Plies are Numbered from Bottom to Top, and the Thermocouples used in Data Acquisition are Numbers 1, 3, 4, 6, 7, 8, 9, 10, 11, 12, 13, and 14 (shown in boldface type).

properties evaluated from this data could directly be compared with the results from the experiments discussed in Section 4.1.

Chapter 5

Results and Discussion

The results of the analysis for the estimation of thermal and kinetic properties are presented and discussed in this chapter. In the first section, the results for the estimation of thermal properties in cured composites from the experiments discussed in Section 4.1 are given. These results include estimates of thermal conductivity perpendicular to the fiber direction and density-specific heat as functions of temperature for two different fiber orientations. The results for the estimation of kinetic properties of the EPON 828 epoxy are presented and discussed in Section 5.2. Section 5.3 is devoted to an analysis of the estimation procedure and experimental design used in the estimation of thermal properties during curing.

5.1 Estimation of Thermal Properties of Cured AS4/EPON 828-mPDA Composite Materials

The thermal properties, effective thermal conductivity perpendicular to the fiber axis and effective density-specific heat, were estimated using the parameter estimation program *PROP1D* from the transient experiments using the cured AS4/EPON 828 composite samples (Section 4.1). Three different aspects of the estimation process were first analyzed to provide insight into the experimental and analytical procedures. These results are presented in Section 5.1.1. The parameter estimates for the experiments

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shown in Table 4.2, in which $[0°]_{24}$ and $[0°,\pm30°,\pm60°,90°]_{2(sym)}$ composite samples were tested, are presented and discussed in Section 5.1.2.

5.1.1 Analysis of the Estimation Procedure

Three important aspects of the estimation procedure were analyzed in detail in this section. The first of these pertains to the residuals, which give insight into experimental errors. This analysis is presented in Section 5.1.1.1. The second aspect of the estimation procedure investigated here relates to the sensitivity coefficients; these results are presented in Section 5.1.1.2. Finally, a discussion is presented on the sequential estimation of the parameters in Section 5.1.1.3.

5.1.1.1 The Residuals

The residuals are defined as the differences between the experimental temperatures and the calculated temperatures using the estimated parameters at corresponding times and locations. Close examination of the residuals can give insight into the adequacy of the experimental design.

The residuals for one typical experiment are presented and discussed here. These results correspond to the second repetition of Exp. 1.9, shown in Table 4.2. In this particular experiment, six thermocouples were used. Three were located at the heated surface (TC #1, TC #2, and TC #3); the fourth and fifth thermocouples (TC #4 and TC #5) were located 3.0 mm and 3.3 mm from the heated surface, respectively, and the sixth thermocouple was used to determine the second boundary condition, which was 7.1 mm from the heated surface. The heat flux was activated ten seconds after the initialization of the experiment. The duration of the heat flux interval was approximately 40 seconds, and the total experimental time was 200 seconds. The residuals of the first two thermocouples, TC #1 and TC #2, and the fifth thermocouple, TC #5, along with the time interval in which the heat flux was activated, are shown in Figure 5.1.

Several observations can be made from this figure. First, the magnitude of the residuals associated with the thermocouples located at the heated surface (TC #1 and TC #2) are highest at the beginning and end of the heat flux interval. The maximum
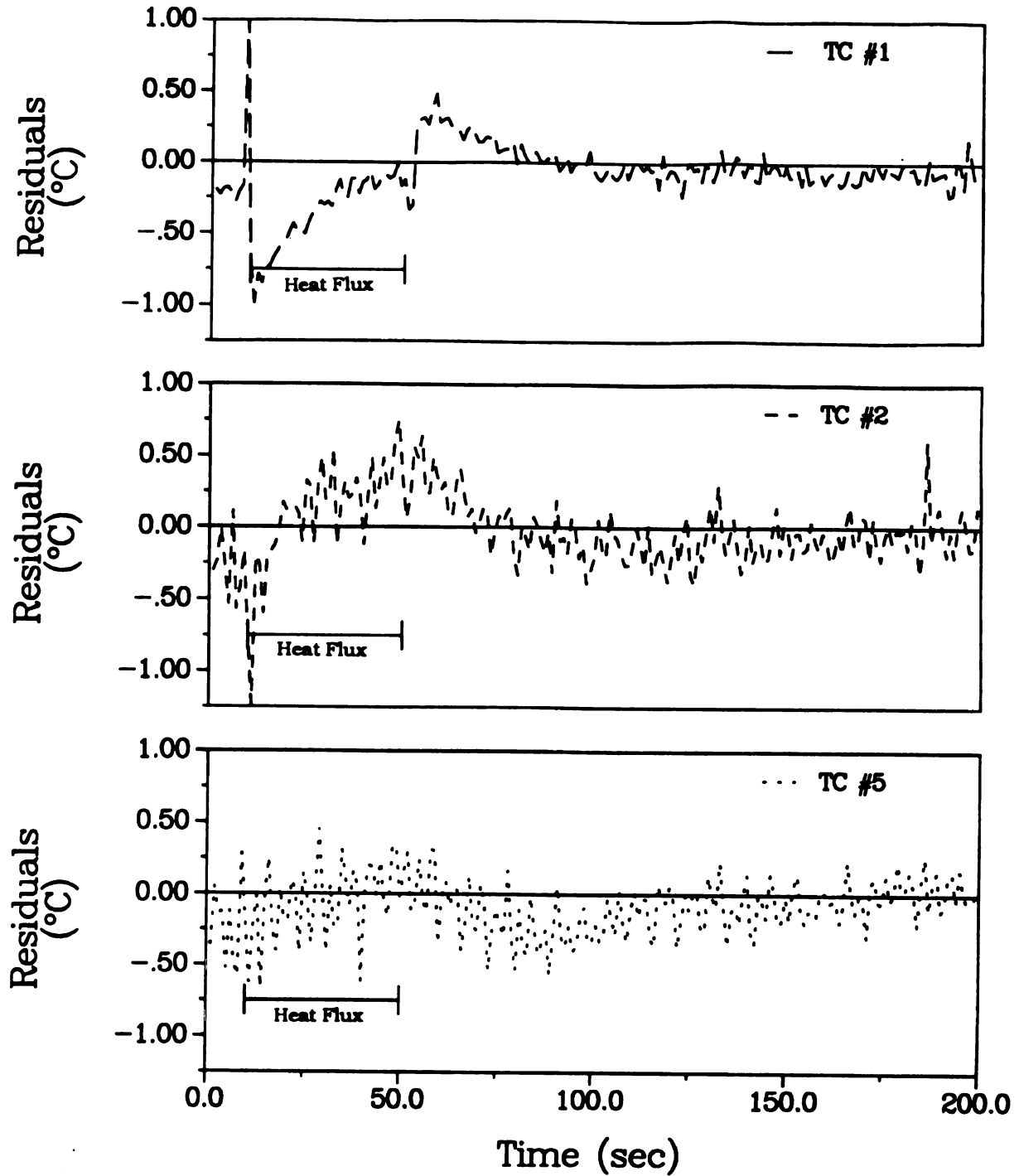
Figure 5.1. Residuals (°C) for Two Thermocouples Located at the Heated Surface (TC #1 and TC #2) and One Thermocouple Located 3.3 mm from the Heated Surface (TC #5) for the Second Repetition of Experiment No. 9 (initial temperature = 100°C).

residual is approximately 1°C, which is approximately 5% of the maximum temperature rise during the experiments. The increase in the magnitude of the residuals at the beginning and end of the heat flux interval was not as pronounced for TC #5, which was located away from the heated surface. Second, the residuals for TC #1 and TC #2 were both biased, but opposite in sign during and immediately after the heating interval. (The residuals for TC #1 are predominantly negative, and the residuals for TC #2 are predominantly positive over this time period.) Also, small biases were observed for the residuals associated with all three thermocouples shown in Figure 5.1 (TC #1, TC #2, and TC #5) and for the two thermocouples not shown in this figure (TC #3 and TC #4) during the second half of the experiment. In all three cases shown in Figure 5.1, these biases were negative, but the biases were observed to be positive for the residuals associated with TC #3 and TC #4.

The high residuals at the beginning and end of the heat flux interval could have resulted from errors in determining the exact time in which the heat flux was activated. As discussed in Section 4.1.3.4, the heater in this experiment was activated manually through use of a timer. Due to the diffusive nature of heat conduction, these errors were not as pronounced for the thermocouple located some distance from the heater (TC#5). Also, finite difference errors tend to be the greatest during step changes in the boundary condition.

The residual bias over the heat flux interval for the heaters located near the surface was most likely due to the placement of the thermocouples with respect to the heater. The heating element in each of the heaters used in these experiments traced back and forth across the heater in rows, leaving a small gap between each row. Therefore, a thermocouple placed directly beneath the heating element would be expected to read higher than the average surface temperature, and a thermocouple placed between the element rows would be expected to read lower than the average surface temperature. This would result in biased residuals, depending on where the thermocouples were located.

The small biases observed for each thermocouple towards the end of the experiment may have been due to improper zeroing of the thermocouples. These experiments

were completed using the Data Translation amplifiers (Section 4.1.3.2) which were very difficult to zero accurately.

Two important points from these observations are that the thermocouples next to the heated surface were the most susceptible to measurement errors and that one major source of errors appeared to be related to the heat flux initialization time.

5.1.1.2 The Sensitivity Coefficients of the Estimated Parameters

The sensitivity coefficients are defined in this case as

$$X_1 = k\left(\frac{\partial T}{\partial k}\right) \qquad \text{and} \qquad X_2 = \rho c_p \left(\frac{\partial T}{\partial \rho c_p}\right)$$

Monitoring each of these values as a function of time can also provide insightful information regarding to the experimental design and the estimated parameters. These sensitivity coefficients are shown in Figure 5.2 for the first and fifth thermocouple locations for the experiment discussed in Section 5.1.1. The first thermocouple location corresponds to TC #1, which was located at the heated surface, and the fifth thermocouple location corresponds to TC #5, which was located 3.3 mm from the heated surface.

The sensitivity coefficients are useful in determining whether or not the estimated parameters are correlated; if the parameters had been correlated, the sensitivity coefficients would have been proportional to each other. From Figure 5.2, the two curves for X_1 and the two curves for X_2 cross over each other and change signs at different times, indicating that the curves are not proportional, and thus implying that the parameters are not correlated.

By definition, the sensitivity coefficients indicate the sensitivity of temperature with respect to small changes in the thermal property values. Thus, relatively higher values of the sensitivity coefficients are desired for parameter estimation. From Figure 5.2, the sensitivity coefficients are approximately zero for the first ten seconds of the
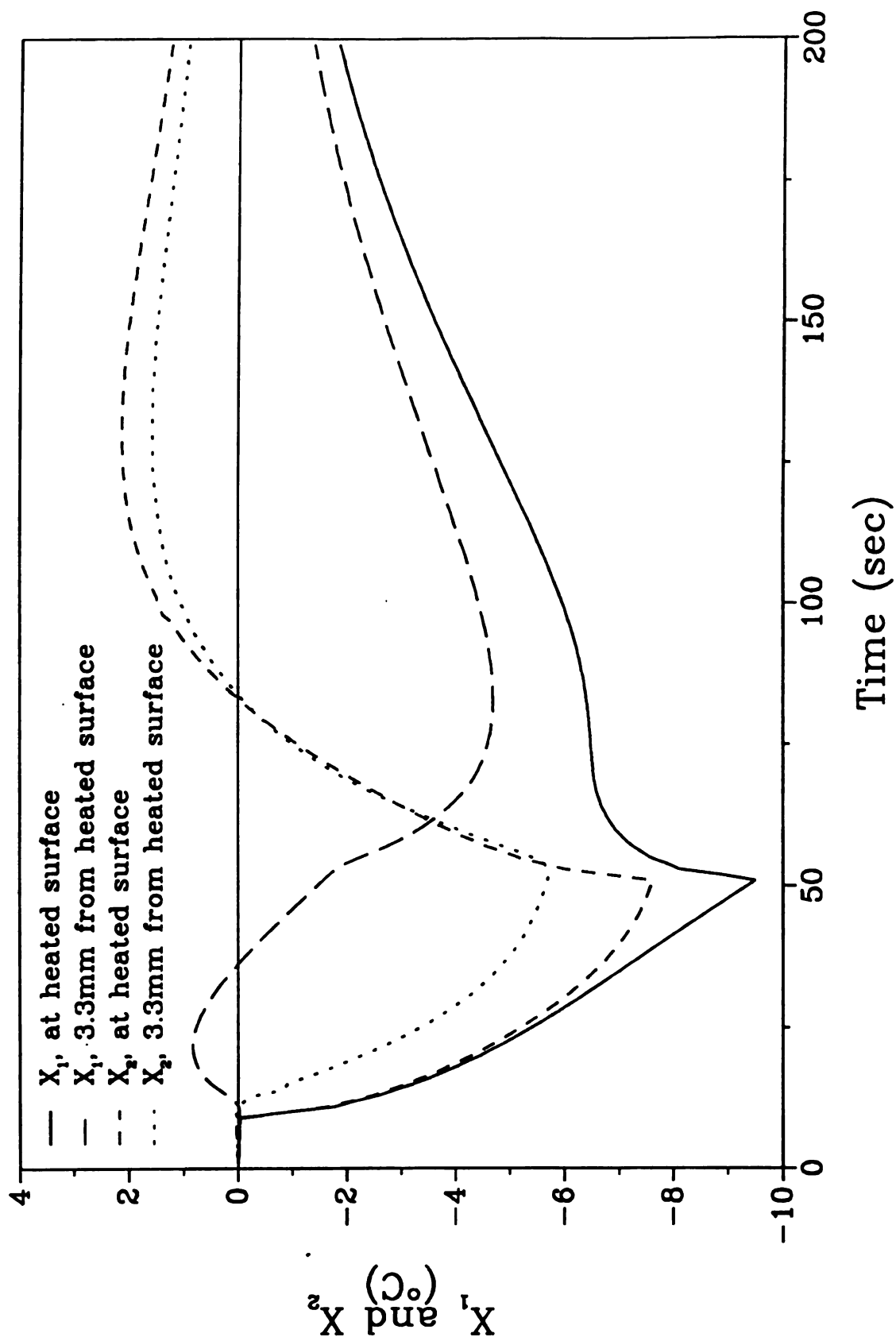
Figure 5.2. Sensitivity Coefficients, X_1 ($k\partial T/\partial k$) and X_2 ($\rho c_p\, \partial T/\partial \rho c_p$), at the Heated Surface and 3.3 mm from the Heated Surface for Second Repetition of Experiment No. 9.

experiment since there was no heat flux over this period. The sensitivity coefficients corresponding to TC #1 (at heated surface) increased in magnitude immediately with the onset of the heat flux, while the responses of the sensitivity coefficients associated with the interior thermocouple (TC #5) were dampened due to the diffusive effects of conduction heat transfer. The magnitudes of the sensitivity coefficients at the heated surface were higher throughout the heating interval (from 10 to 50 seconds), at which time they experienced a sharp decrease in magnitude. The sensitivity coefficients at the interior location also diminished after the heating interval, but in this case, the response was delayed.

From these observations, the sensitivity coefficients at the heated surface provided the most information with regards to the estimation of the parameters.

5.1.1.3 The Sequential Estimates of the Estimated Parameters

Investigation of the sequential parameter estimates is also useful in evaluating an experimental design. The sequential estimates of thermal conductivity, k, and density-specific heat, ρc_p, for the experiment discussed in Section 5.1.1 are shown in Figure 5.3. The heat flux was activated ten seconds after the beginning of the experiment. The estimated parameters fluctuated greatly over this period, with some values off the scale shown in Figure 5.3. These values can be disregarded since no information was available from the measurements. (As discussed in the the previous section, the sensitivity coefficients equaled zero during the first ten seconds.) The estimates for both thermal conductivity and density-specific heat were constant after approximately 130 seconds, indicating that additional data would have provided little additional information for the estimation of the parameters; also it indicates that the heat conduction model is satisfactory.

5.1.1.4 Insights into the Experimental Design

The observations discussed in Sections 5.1.1.1, 5.1.1.2, and 5.1.1.3 are summarized here. One important observation was that the thermocouples closest to the heated surface provided the most information for parameter estimation, however, these
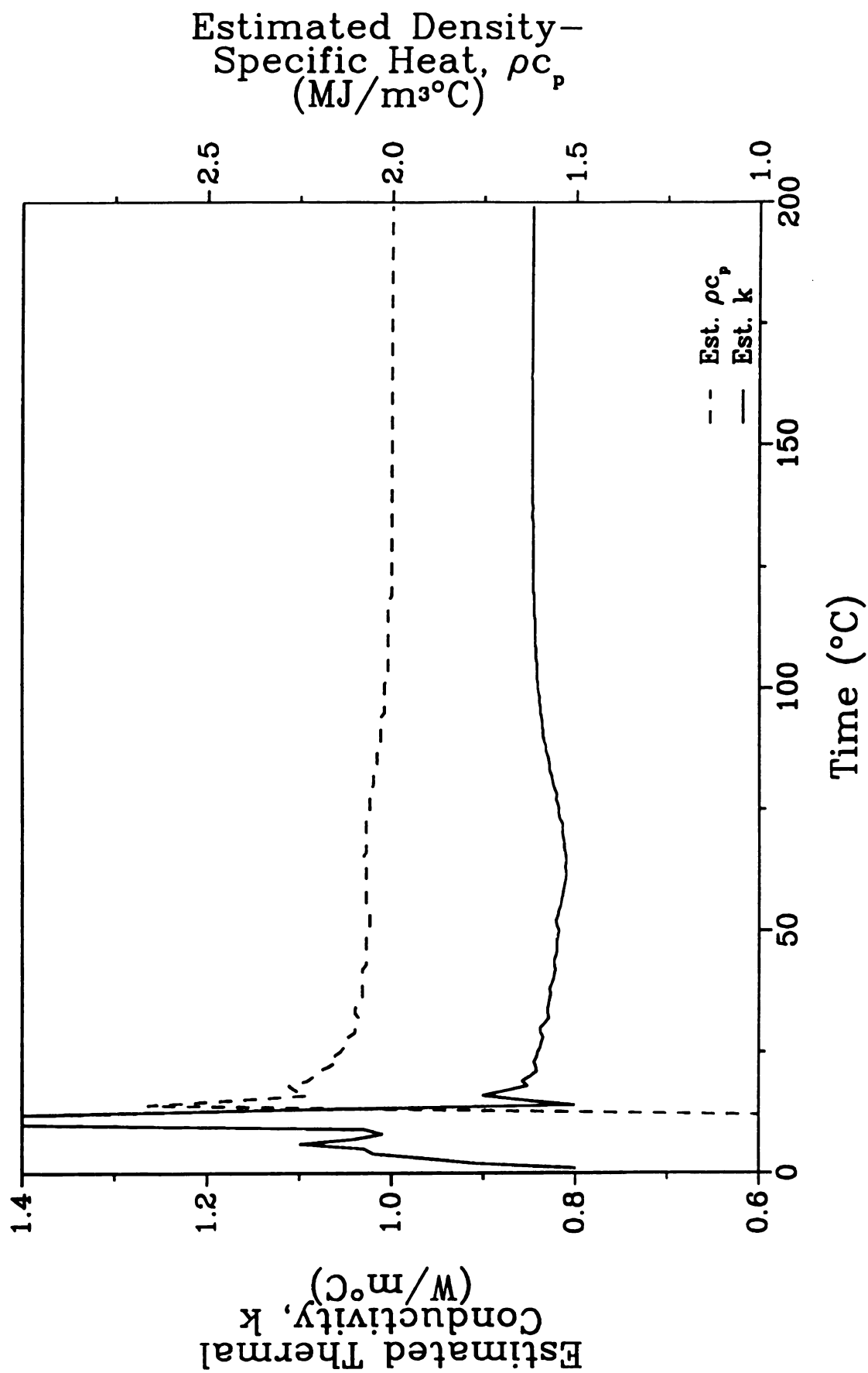
Figure 5.3. Sequential Estimation of Thermal Conductivity, k, and Density Specific Heat, ρc_p, from the Second Repetition of Experiment No. 9 (initial temperature $\approx$ 100°C).

thermocouples were also the most sensitive to experimental errors. In addition, at least two thermocouples were required at the heated surface to account for the variations in temperature due to the location of the heating element within the heater. Finally from the analysis of the sequential parameter estimates, the total experimental time of 200 seconds appeared to be satisfactory.

5.1.2 Estimation of Thermal Conductivity and Density-Specific Heat of Cured AS4/EPON 828 Composite Materials

The thermal properties, thermal conductivity and density-specific heat were estimated using the procedures presented in Section 3.1 for each repetition of the experiments discussed in Section 4.1.5 and shown in Table 4.2. The results of this estimation procedure are presented in this section. First, results for the experiments using the $[0°]_{24}$ samples are given and discussed in Section 5.1.2.1, and then the results for the experiments using the $[0°,\pm30°,\pm60°,90°]_{2(sym)}$ samples are presented and discussed in Section 5.1.2.2. A comparison of these results is given in Section 5.1.2.3, and finally, the results from this study are compared to previously published data in Section 5.1.2.4.

5.1.2.1 Experiments using $[0°]_{24}$ Samples

The results for the thermal properties, namely the estimated effective thermal conductivity perpendicular to the fiber axis and the estimated effective density-specific heat product, of the cured $[0°]_{24}$ AS4/EPON 828 composite samples are given for the experiments with approximate initial temperatures of 25°C, 50°C, 75°C, 100°C, and 125°C in Tables C.1-C.5 (Appendix C), respectively. These results include the root mean squared errors, which were based on the difference between the experimental and calculated temperatures using the estimated thermal properties. In each of these experiments, five or six thermocouples were used, and at least two were located at the heated surface.

The results from each repetition of each experiment were averaged, and the averaged property estimates are given in Table 5.1. In each case, the total number of

Table 5.1. Averaged Estimated Values and 95% Confidence Intervals for Effective Thermal Conductivity, k, Perpendicular to the Fiber Axis and Effective Density-Specific Heat, ρc_p, of Cured $[0°]_{24}$ AS4/EPON 828-mPDA Composites.

Exper. No.[a]	No. of Repet.	Avg. Temp. Range (°C)	$\bar{k}$ (W/m°C)	$\overline{\rho c_p}$ (kJ/m³ °C)
1.1	9	25 – 52	0.797±0.014	1,580±10
1.6	6	27 – 46	0.797±0.007	1,570±30
1.11	6	26 – 46	0.745±0.014	1,560±10
1.1, 1.6 1.11	**21**	**26 – 48**	**0.782±0.013**	**1,570±10**
1.2	6	53 – 75	0.793±0.006	1,650±20
1.7[b]	12	50 – 68	0.868±0.010	1,680±20
1.12	6	52 – 72	0.790±0.021	1,600±30
1.2, 1.12	**12**	**52 – 72**	**0.791±0.009**	**1,630±20**
1.3	6	78 – 98	0.810±0.012	1,690±20
1.8[b]	6	75 – 91	0.918±0.009	1,810±30
1.13	6	77 – 95	0.797±0.020	1,760±15
1.3, 1.13	**12**	**77 – 95**	**0.803±0.010**	**1,730±30**
1.4	12	102 – 120	0.832±0.015	1,900±50
1.9[b]	6	100 – 115	0.971±0.015	1,960±30
1.14	6	100 – 115	0.816±0.008	1,830±30
1.4, 1.14	**18**	**101 – 117**	**0.826±0.010**	**1,880±40**
1.5	9	127 – 145	0.880±0.040	2,050±80
1.10[b]	6	126 – 141	1.011±0.010	2,090±30
1.15	6	126 – 140	0.874±0.007	1,930±30
1.5, 1.15	**15**	**126 – 142**	**0.877±0.020**	**2,000±50**

a. Experiment numbers refer to those in Table 4.2.
b. Samples preheated to 150°C; not used in boldface average values.

repetitions, the average temperature range of the experiments, the average effective thermal conductivity perpendicular to the fiber axis, and the average effective density-specific heat are given, along with the 95% confidence intervals of the estimated parameters. The 95% confidence intervals were calculated using the estimated standard deviation of the averaged values and the t-distribution (Walpole and Meyers, 1978).

The averaged parameter estimates within the different temperature levels were then compared. In the experiments initially at approximately 25°C (Exp. 1.1, 1.6, and 1.11 in Table 5.1), the 95% confidence intervals for the estimated thermal conductivities of Exp. 1.1 and 1.6 overlapped one another, but the 95% confidence interval for Exp. 1.11 was slightly lower. The 95% confidence intervals for density-specific heat overlapped each other for all three cases, indicating that statistically, the means were equivalent.

The composite samples in Exp. 1.7, 1.8, 1.9, and 1.10, with corresponding initial temperatures of approximately 50°C, 75°C, 100°C and 125°C, were accidentally heated to 150°C for two hours prior to the experiments. This is above the glass transition temperature of the epoxy, which is approximately 135°C to 150°C, depending on the heating rate. (The glass transition temperature increases with increased heating rates.) The glass transition temperature is the temperature at which the molecules in the amorphous phase (epoxy) begin to rotate, and at this temperature, the material begins to change from a glassy structure to a rubbery structure (Sichina, 1989). (There is, however, no visible change in the epoxy.) It is evident that these changes effected the epoxy even after the samples were cooled, when comparing the 95% confidence intervals of the estimated parameters at each temperature interval. In all cases, the 95% confidence intervals of the effective thermal conductivities estimated for Exp. 1.7, 1.8, 1.9, and 1.10 were higher than the other two corresponding experiments at each temperature interval. One explanation for the increased thermal conductivity is that the rotation of the molecules facilitated better bonding along the matrix fiber interface after the composite had cooled, and therefore, increased the contact conductance between

the fiber and the epoxy matrix. Although the mean estimates of the effective density-specific values were higher for Exp. 1.7, 1.8, 1.9, and 1.10, than for the other experiments at the same temperature intervals, the 95% confidence intervals were higher only for Exp. 1.8, in which the initial temperature was approximately 75°C.

Comparing the parameter estimates for the experiments not preheated to 150°C at each of the four temperature levels above 25°C (50°C, 75°C, 100°C, and 125°C), the 95% confidence intervals of the estimated thermal conductivity values overlapped one another within each temperature level. The 95% confidence intervals of the density-specific heat estimates did not overlap, however, for the experiments with initial temperatures at 75°C and 125°C.

The estimated thermal properties for Exp. 1.1 , 1.6, and 1.11 (~25°C), Exp. 1.2 and 1.12 (~50°C), Exp. 1.3 and 1.13 (~75°C), Exp. 1.4 and 1.14 (~100°C), and Exp. 1.5 and 1.15 (~125°C) were combined at each temperature level, and the combined results, along with their respective confidence intervals are indicated by the boldface type in Table 5.1. Note that the results from the samples preheated to 150°C were not included in these values. The combined results clearly indicate that both thermal conductivity and density-specific heat estimates increase with temperature.

The experiments conducted above 125°C approached the glass transition temperature, which may have affected some of the estimated parameters, even though the sample achieved these temperatures for only a few seconds near the surface of the sample. From Table C.5 (Appendix C), the estimates for thermal conductivity perpendicular to the fibers increased with each successive repetition in Exp. 1.5; however, this did not hold true for the repetitions in Exp. 1.15. Therefore, it is difficult to conclude whether or not the glass transition temperature had any effect on the parameter estimates based on these observations.

It was desired to associate the estimated parameters values with discrete temperature values, but this was difficult since each experiment was conducted over a temperature range rather than at single temperature, and because of the temperature variation within the experimental samples. For convenience, the estimated parameters

were associated with the average surface temperature next to the heater from each experiment, and the estimated thermal conductivity and density-specific heat values given in Tables C.1-C.5 are plotted against these temperatures in Figures 5.4 and 5.5, respectively.

A linear regression curve was fit through the estimated thermal conductivity values from Exp. 1.1-1.6, shown in Figure 5.4. The regression line and the 95% confidence band of this curve are indicated by the solid lines. A second regression curve was determined for the estimated thermal conductivity values from Exp. 1.7-1.10 in which samples were preheated to 150°C for two hours; this regression line and the associated confidence band are indicated by the medium dashed lines. These two regression lines are independent of one another since their respective confidence bands do not overlap one another. A third regression line (short dashed line) is shown for the data from Exp. 1.1-1.4, 1.6, and 1.11-1.15; this curve does not include data from the experiments initializing at approximately 125°C, in which the sample may have exceeded the glass transition temperature for a few seconds in each experiment. The confidence band for this curve overlaps the confidence band for the first regression line which included the experiments above 125°C, indicating that there is no significant difference between these two curves.

The parameter estimates for density-specific heat were analyzed and plotted in a similar matter, and the results from the linear regression analysis are also shown in Figure 5.5. The 95% confidence bands of the linear regression curves associated with Exp. 1.1-1.6 and 1.11-1.15 (solid lines) and Exp. 1.7-1.10 (medium dashed lines) did not overlap, indicating that these regression lines are independent, as was found for the thermal conductivity curves. The confidence bands for the regression line which did not incorporate the data above 125°C (short dashed lines) overlapped the bands which did include this data (solid lines), indicating that, as for the case for thermal conductivity, the regression lines were the statistically the same.

The estimated effective thermal conductivity perpendicular to the fiber axis and the effective density-specific heat values can be expressed as functions of temperature from the linear regression curves in Figures 5.4 and 5.5 as:
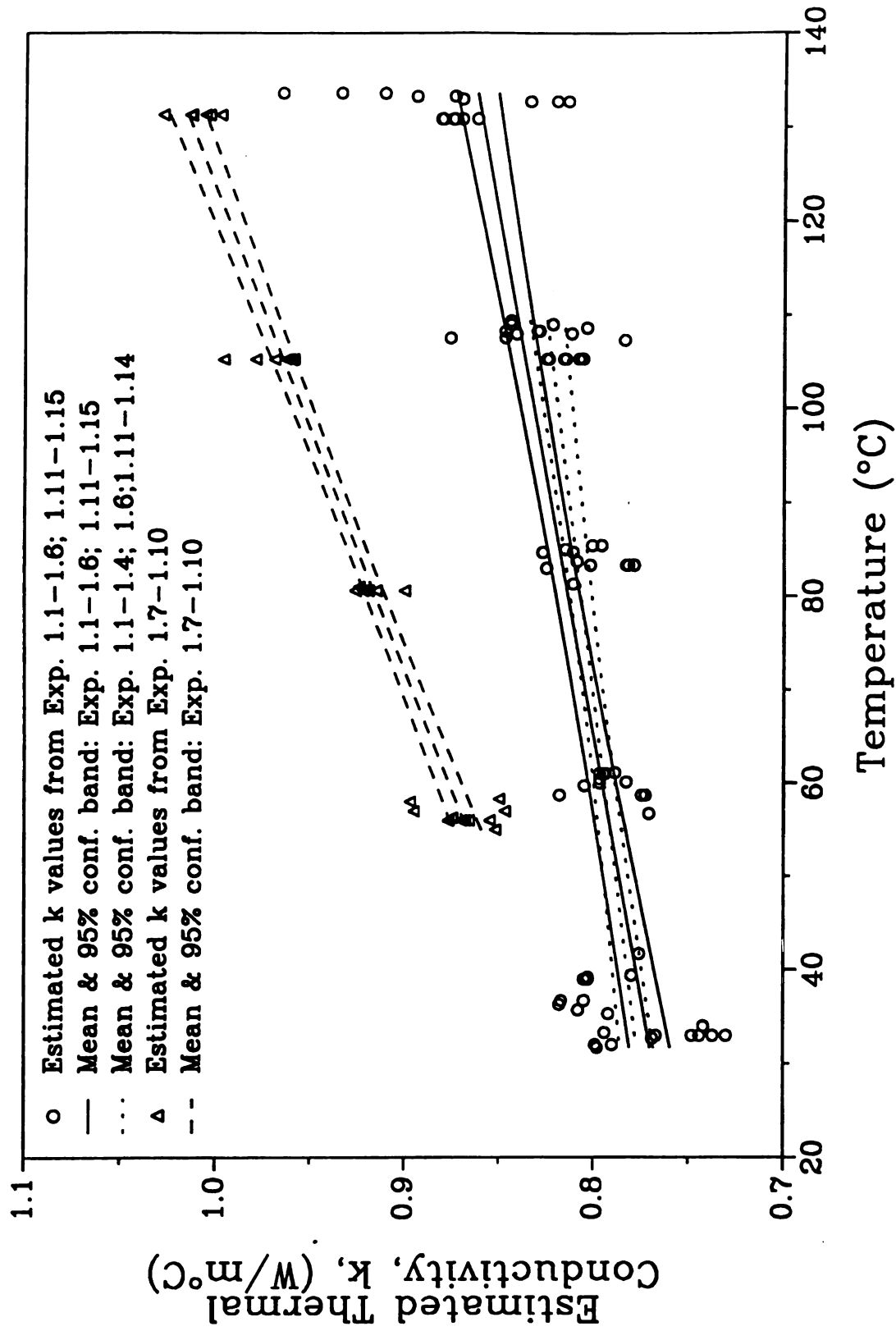
Figure 5.4. Estimation of Effective Thermal Conductivity Perpendicular to the Fiber Axis, k, of Cured [0°]₂₄ AS4/EPON 828-mPDA Composites.
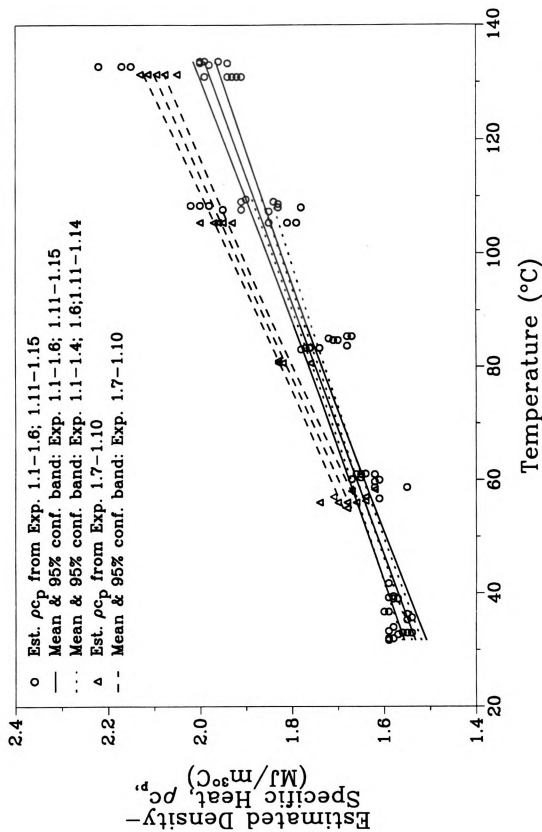
Figure 5.5. Estimation of Effective Density-Specific Heat, ρc_p, of Cured $[0^\circ]_{24}$ AS4/EPON 828-mPDA Composites.

$$k(T) = k_0 + k_1 T \qquad\qquad (5.1a)$$

for thermal conductivity, and,

$$\rho c_p(T) = (\rho c_p)_0 + (\rho c_p)_1 T \qquad\qquad (5.1b)$$

for density-specific heat. The regression parameters (k_0, k_1, $(\rho c_p)_0$ and $(\rho c_p)_1$) and their associated 95% confidence intervals are given in Table 5.2.

5.1.2.2 Experiments using $[0°,\pm30°, \pm60°, 90°]_{2(sym)}$ Samples

Results, including the estimated effective thermal conductivity values perpendicular to the fibers and the estimated effective density-specific heat values, for each repetition of the experiments using cured $[0°,\pm30°, \pm60°, 90°]_{2(sym)}$ samples with initial temperatures of approximately 25°C, 50°C, and 75°C are given in Tables C.6-C.8 (Appendix C), respectively.

Averaged repetition values for each experiment are given in Table 5.3. In each case, the average thermal conductivity and density-specific heat values are given, along with the 95% confidence intervals of the averaged parameters, the total number of repetitions averaged, and the average temperature range of the experiments.

The average parameter estimates for each experiment within each different temperature level were again compared. At each temperature interval, the confidence intervals of the density-specific heat overlapped one another, but the confidence intervals of the thermal conductivity values did not. The differences in the values for thermal conductivity may have been the result of the different processing methods used to cure the samples. Since, from Figure 5.2, the sensitivity coefficients evaluated closest to the heater were the highest in magnitude, the thermocouples at these locations had the greatest influence on the estimates of the thermal conductivity. Therefore, in Exp. 1.16, 1.17, 1.18, the estimates of the parameters had the greatest influence from the samples cured in the hydraulic press, since these sample plates were closest to the heated surface. Likewise, the samples cured in the autoclave had the

Table 5.2. Estimated Parameters and 95% Confidence Intervals for the Linear Regression of Both Effective Thermal Conductivity, k, Perpendicular to the Fibers and Effective Density-Specific Heat, c, with Temperature of Cured $[0°]_{24}$ AS4/EPON 828-mPDA Composites.

Thermal Conductivity		$k = k_0 + k_1 T$	
Figure Number	Experiment Numbers	k_0 (W/m°C)	k_1 (W/m(°C)^2)
5.4	1.1-1.6; 1.11-1.15	0.742±0.015	$(0.902±0.173)10^{-3}$
5.4	1.1-1.4; 1.6; 1.11-1.15	0.758±0.014	$(0.615±0.183)10^{-3}$
5.4	1.7-1.10	0.760±0.016	$(1.943±0.175)10^{-3}$
5.6	1.16-1.21	0.689±0.038	$(0.877±0.642)10^{-3}$
Density-Specific Heat		$\rho c_p = (\rho c_p)_0 + (\rho c_p)_1 T$	
Figure Number	Experiment Numbers	$(\rho c_p)_0$ (MJ/m^3 °C)	$(\rho c_p)_1$ (MJ/m^3 (°C)^2)
5.5	1.1-1.6; 1.11-1.15	1.390±0.034	$(0.450±0.039)10^{-2}$
5.5	1.1-1.4; 1.6; 1.11-1.15	1.407±0.033	$(0.419±0.043)10^{-2}$
5.5	1.7-1.10	1.362±0.038	$(0.562±0.042)10^{-2}$
5.7	1.16-1.21	1.588±0.092	$(0.187±0.154)10^{-2}$

Table 5.3. Averaged Estimated Values and 95% Confidence Intervals for Effective Thermal Conductivity, k, Perpendicular to the Fiber Axis and Effective Density-Specific Heat, ρc_p, of Cured $[0°,\pm30°,\pm60°,90°]_{2(sym)}$ AS4/EPON 828-mPDA Composites.

Exper. No.[a]	No. of Repeti.	Avg. Temp. Range (°C)	$\bar{k}$ (W/m°C)	$\overline{\rho c_p}$ (kJ/m³ °C)
1.16	11	27 - 41	0.687±0.017	1,680±70
1.19	6	28 - 51	0.767±0.037	1,600±40
1.16, 1.19	**17**	**27 - 46**	**0.715±0.025**	**1,660±50**
1.17	6	53 - 71	0.716±0.009	1,650±20
1.20	6	52 - 75	0.786±0.020	1,690±20
1.17, 1.20	**12**	**52 - 74**	**0.751±0.025**	**1,670±20**
1.18	6	76 - 97	0.744±0.008	1,710±20
1.21	6	78 - 97	0.767±0.061	1,820±220
1.18, 1.21	**12**	**77 - 97**	**0.756±0.026**	**1,770±90**

a. Experiment numbers refer to those in Table 4.2.

greatest influence on the parameters estimates for Exp. 1.19, 1.20, and 1.21. At each temperature level, the estimated thermal conductivities which had the greatest influence from the autoclave cured samples were higher than the estimated parameters which had the greatest influence from the samples cured in the press. One explanation for the higher thermal conductivity values is that the autoclave provided a more uniform pressure distribution with time throughout the curing process, thus providing better bonding between the epoxy matrix and the fibers. It is expected that these differences would be greater when the fibers are multi-directional, as they were in this case, since during the experimental stacking procedure, it was observed that the fibers tended to side over each other when they were stacked at different angles.

The average results for each experiment were combined at each temperatures interval. These values, along with the associated 95% confidence intervals are indicated by the boldface type in Table 5.3. As was observed for the results using the $[0°]_{24}$, both the estimated thermal conductivity and density specific heat values increased with temperature. The estimated thermal conductivity and density-specific heat values are shown versus the average surface temperature in each experiment in Figure 5.6 and 5.7, respectively. A linear regression curve was fit through the estimates in each of these figures using PLOTit[R] (1989) software, and these curves, along with their associated 95% confidence bands are indicated by the solid lines. The estimated parameters associated with these linear regression curves (see eq. 5.1a,b) are also shown in Table 5.2.

5.1.5.3 Comparison of Results from $[0°]_{24}$ and $[0°,\pm30°, \pm60°, 90°]_{2\,(sym)}$ Samples

The linear regression curves indicated by the solid lines in Figures 5.4 and 5.6 for thermal conductivity, and by the solid lines in Figures 5.5 and 5.7 for density-specific heat are compared in Figures 5.8 and 5.9, respectively. The curves in Figure 5.8 for thermal conductivity are clearly independent; one explanation for these differences is that there is better bonding between the laminates stacked with the plies oriented in the same direction than when the ply angle is changed. Poorer bonding would decrease the
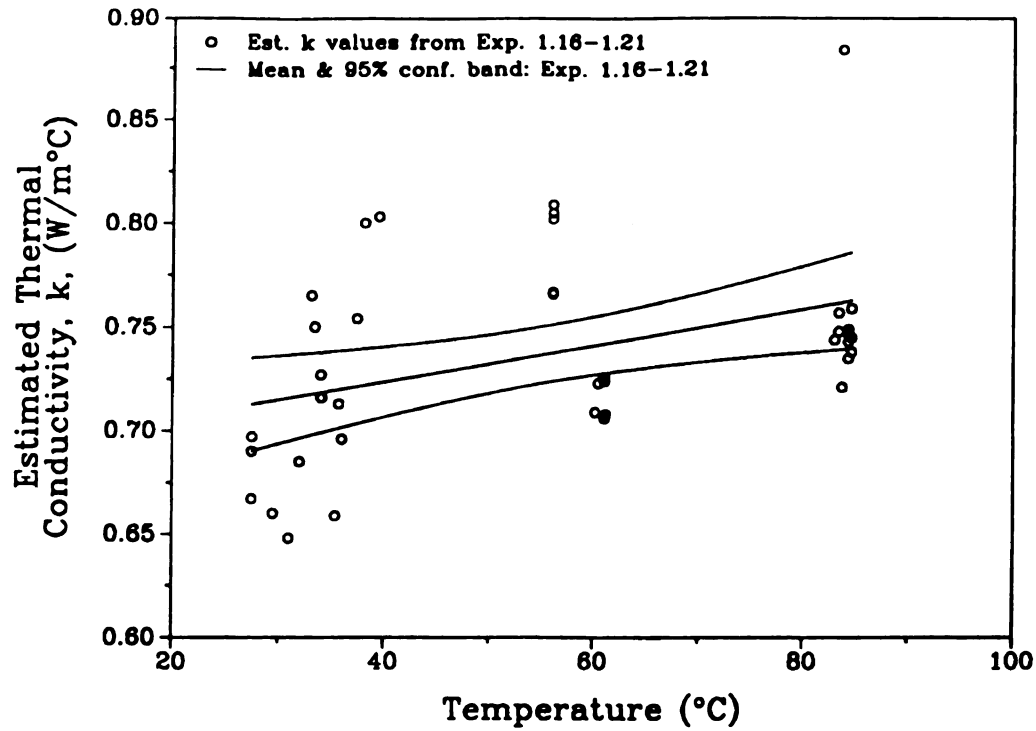
Figure 5.6. Estimation of Effective Thermal Conductivity Perpendicular to the Fiber Axis, k, of Cured [0°, ±30°, ±60°, 90°]$_{2(sym)}$ AS4/EPON 828-mPDA Composites.
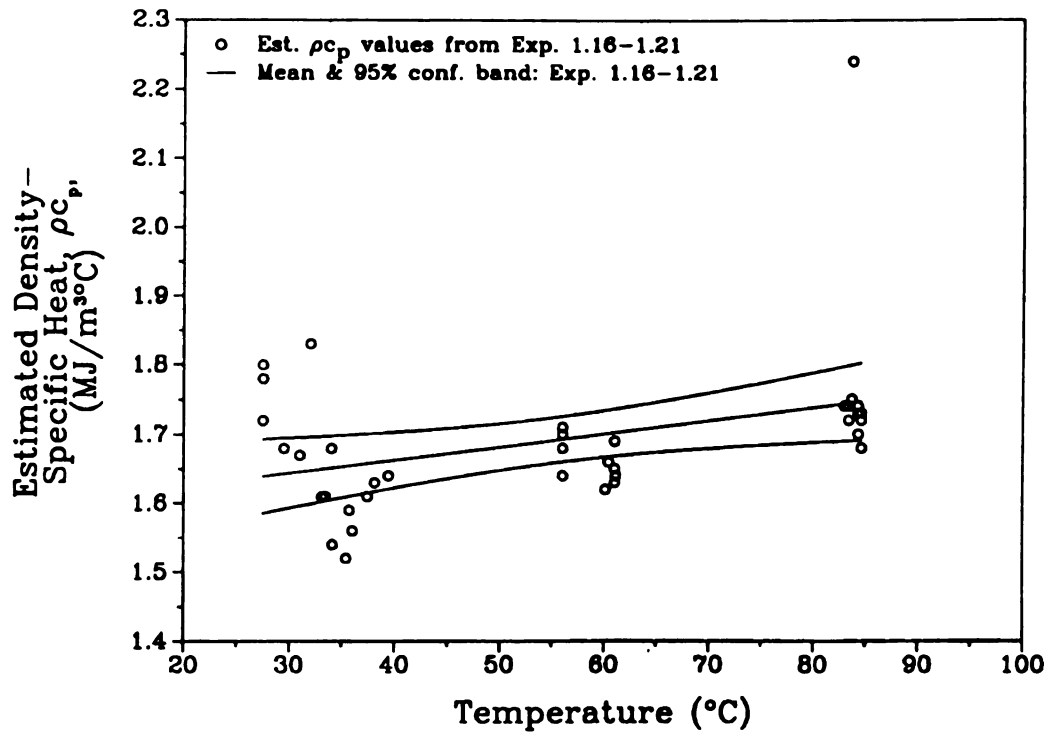
Figure 5.7. Estimation of Effective Density-Specific Heat, ρc_p, of Cured [0°, ±30°, ±60°, 90°]$_{2(sym)}$ AS4/EPON 828-mPDA Composites.
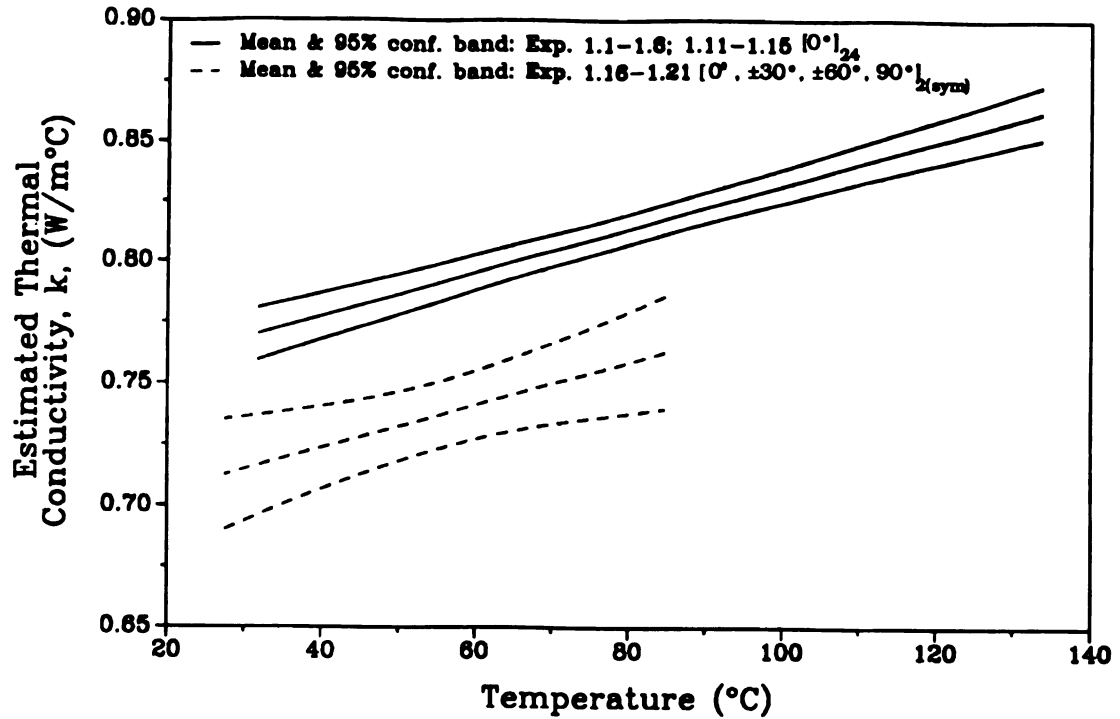
Figure 5.8. Comparison of Linear Regression Curves for Effective Thermal Conductivity Perpendicular to the Fiber Axis, k, of Cured $[0°]_{24}$ and Cured $[0°, ±30°, ±60°, 90°]_{2(sym)}$ AS4/EPON 828-mPDA Composites.
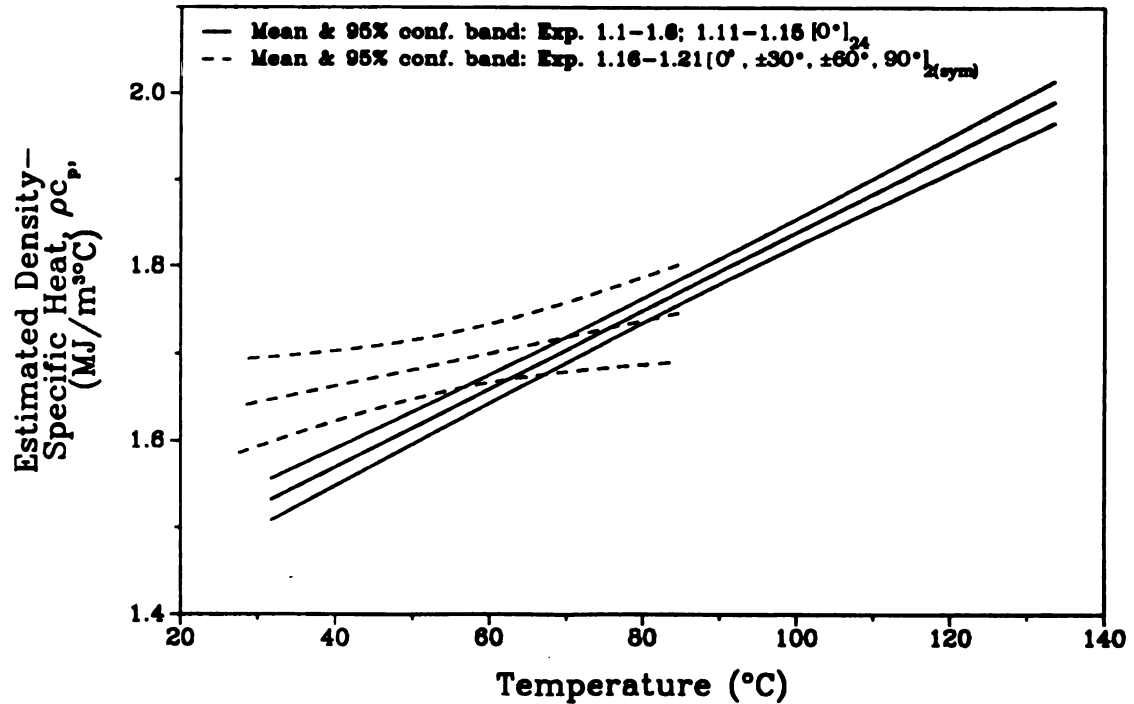
Figure 5.9. Comparison of Linear Regression Curves for Effective Density-Specific Heat, ρc_p, of Cured $[0°]_{24}$ and Cured $[0°, ±30°, ±60°, 90°]_{2(sym)}$ AS4/EPON 828-mPDA Composites.

thermal contact conductance between the ply interfaces and reduce the resulting effective thermal conductivity perpendicular to the fiber direction. The differences between the density specific heat curves in Figure 5.9 are not as evident since the two curves overlap one another from approximately 55°C to 85°C. It was not expected that the stacking sequence would alter the density-specific heat values.

5.1.5.4 Comparison with Previously Published Results

The estimated thermal conductivity values perpendicular to the fiber axis using [0°] oriented samples are compared to previously published results on comparable fiber-epoxy systems in Table 5.4. At 20°C, the results in this study were within the 95% confidence interval of the results presented by Loh (1989), and since the confidence interval for the results by Ishikawa (1980) are not given, it can not be said with any certainty whether or not these estimates are comparable. The results of Loh (1989) at 100°C were 12% higher than those found in this study.

5.2 Estimation of Kinetic Parameters Associated with the Curing of EPON 828/mPDA Epoxy

In this section, the results from the differential scanning calorimetry (DSC) experiments used to characterize the curing of an EPON 828/mPDA epoxy system are given. The total heat of reaction was first found from the dynamic DSC experiments, and then the degree of cure was calculated for each isothermal DSC experiment shown in Table 4.4; these results are presented and discussed in Section 5.2.1. The first half of the cure was evaluated with the assumption that the reaction rate was limited by autocatalyzation, and the second half of the cure was analyzed with the assumption that the reaction rate was controlled by diffusion. Three different models were evaluated for the first half of the cure; estimates for the kinetic parameters using these models are presented and compared with previously published results on similar epoxy systems in Section 5.2.2. In addition, estimates are given for the parameters associated with the model shown in eq. (3.18) for the last half of the cure in Section 5.2.3. Finally,

Table 5.4.   Comparison of Estimated Effective Thermal Conductivity
Perpendicular to the Fiber Axis, k, with Previously Published Results.

Composite Material	Temp. (°C)	k (W/m°C)	Estimation Method	Reference
Carbon/ 3130 Epoxy[a]	20	0.72	Infrared Radiation Method	Ishikawa (1980)
AS4 Carbon/ Epon 828	20 100	0.80±0.02 0.93±0.02	Gauss Minimization	Loh (1989)
AS4 Carbon/ Epon 828	20 100	0.76±0.02 0.83±0.03	Gauss Minimization	present study Exp. 1.1-1.6; 1.11-1.15

a.   Similar in structure to Epon 828 epoxy, with similar thermal conductivity
(Ishikawa (1980).

the models and the associated parameters estimates selected for use in procedures for the estimation of thermal properties during curing are presented in Section 5.2.4.

5.2.1 Determination of the Total Heat of Reaction and Degree of Cure

The total heat of reaction (eq. 3.9) was required to determine the degree of cure (eq. 3.8) from the isothermal differential scanning calorimetry (DSC) experiments. The total heat of reaction was first determined from the dynamic DSC experiments as described in Section 4.2. In each of these experiments, a constant base-line was established, and the magnitude of the baseline was subtracted from the experimental data. The modified data was integrated over time using the DuPont Thermal Analysis System 9900 software to determine the total heat of reaction. The total heat of reaction values calculated for the eight dynamic experiments shown in Table 4.4, along with the average heat of reaction from all the experiments, are shown in Table 5.5.

The degree of cure was then determined for each isothermal experiment conducted at 60°C, 70°C, 100°C, and 110°C (Table 4.4). The isothermal DSC data was post processed as discussed in Section 4.2.2.3 to obtain heat of reaction rate values for each isothermal experiment. These values were then transferred to a VAXstationII/GPX microcomputer, where the cumulative heat of reaction was determined as a function of time through numerical integration of the heat of reaction rates with time, and the degree of cure was calculated by dividing the cumulative heat of reaction values by the average total heat of reaction shown in Table 5.5.

These degree of cure values, which vary with time, for the various isothermal experiments were then used to estimate the kinetic parameters in the kinetic models shown in eqs. (3.4-6).

5.2.2 Parameter Estimation for Autocatalyzed Cure Kinetics (no Diffusion)

The degree of cure data less than 0.50 were assumed to follow an autocatalyzed kinetic reaction without any influence from decreased molecular mobility. The use of 0.50 as a limit for the autocatalyzed controlled reactions is based on the observations

Table 5.5. Total Heat of Reaction Calculated from Dynamic Differential Scanning Calorimetry Experiments (Exp. 2.1) using EPON 828/mPDA Epoxy.

Repetition No.	Heat of Reaction (J/kg)
1	0.459
2	0.444
3	0.468
4	0.452
5	0.432
6	0.451
7	0.439
8	0.447
Average	0.449±0.009

by Sourour and Kamal (1976) as discussed in Section 2.2.3, and on similar observations in this study. The degree of cure data was first used to determine the kinetic parameters (i.e. rate constants) at the different experimental temperatures associated with the kinetic models shown in eqs. (3.4-3.6), and then the estimated parameters were used to determine the activation energy constants and the pre-exponential factors in eq. (3.7).

5.2.2.1 Estimation of Rate Constants and Exponents

The rate constants and exponents in each of the kinetic models shown in eqs. (3.4-3.6) were first determined for each of the isothermal DSC experiments shown in Table 4.4. These experiments were conducted at $60°C$, $70°C$, $100°C$, and $110°C$, with three repetitions at each temperature. In these analyses, all linear regression calculations were performed using PLOTit^R (1989) software.

In eq. (3.4), the parameters to be estimated were the rate constants, c_1 and c_2, and the exponential, m. These parameters were estimated from the initial and maximum degree of cure rate data from each experiment, using the method given by Ryan and Dutta (1979) and outlined in eqs. (3.10-3.13). The least squares method discussed in Section 3.2.1 and shown in eq. (3.14), was also used to determine these parameters. In this method, the parameters were estimated from all of the degree of cure data in each experiment through the minimization of a least squares function. The estimated values for c_1, c_2, and m, using the Ryan and Dutta method and the least squares method are shown in Tables 5.6 and 5.7, respectively. In addition, 95% confidence intervals are given for the rate constants estimated using the alternate approach.

The isothermal DSC data were then used to determine the rate constants, c_1 and c_2 in eq. (3.5), using the method given by Sourour and Kamal (1976) and discussed in Section 3.2.1. The estimated rate constants and their respective 95% confidence intervals are shown in Table 5.8 for each isothermal DSC experiment shown in Table 4.4.

The rate constant, c_1, and the exponential, n, from the model shown in eq. (3.6) were also evaluated from the isothermal DSC data. These parameters were determined

Table 5.6. Rate Constants, c_1 and c_2, and Exponent, m, Determined from eq. (3.4) and Degree of Cure Values, α, Less than 50% for EPON 828/mPDA Epoxy, using the Ryan and Dutta (1979) Method.

Exper. No.	Rep. No.	Temp. (°C)	Ryan and Dutta Method		
			c_1 (s^{-1})	c_2 (s^{-1})	m
2.2	1	60	3.06E-5	3.70E-4	0.809
	2	60	3.04E-5	3.43E-4	0.817
	3	60	1.86E-5	3.51E-4	0.777
2.3	1	70	4.27E-5	6.01E-4	0.797
	2	70	5.33E-5	6.05E-4	0.815
	3	70	6.02E-5	5.29E-4	0.848
2.4	1	100	2.40E-4	2.36E-3	0.757
	2	100	2.92E-4	2.37E-3	0.749
	3	100	2.60E-4	2.12E-3	0.727
2.5	1	110	3.97E-4	3.81E-3	0.793
	2	110	4.56E-4	3.65E-3	0.705
	3	110	3.02E-4	3.61E-3	0.668

a. Experiment numbers and repetition numbers refer to those in Table 4.4

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Table 5.7. Rate Constants, c_1 and c_2, and Exponent, m, and Associated 95% Confidence Intervals, Determined from eq. (3.4) and Degree of Cure Values, α, less than 50% for EPON 828/mPDA Epoxy, using a Least Squares Method.

Exper. No.[a]	Rep. No.[a]	Temp. (°C)	Alternate Method		
			c_1 (s^{-1})	c_2 (s^{-1})	m
2.2	1	60	$(2.22\pm0.12)E-5$	$(2.46\pm0.05)E-4$	0.832
	2	60	$(2.31\pm0.08)E-5$	$(2.27\pm0.02)E-4$	0.834
	3	60	$(1.55\pm0.08)E-5$	$(2.30\pm0.03)E-4$	0.781
2.3	1	70	$(3.46\pm0.17)E-5$	$(3.92\pm0.06)E-4$	0.816
	2	70	$(4.06\pm0.22)E-5$	$(4.02\pm0.08)E-4$	0.847
	3	70	$(5.33\pm0.40)E-5$	$(3.36\pm0.16)E-4$	0.880
2.4	1	100	$(1.76\pm0.20)E-4$	$(1.59\pm0.07)E-3$	0.765
	2	100	$(1.59\pm0.36)E-4$	$(1.57\pm0.12)E-3$	0.691
	3	100	$(1.58\pm0.22)E-4$	$(1.45\pm0.07)E-3$	0.731
2.5	1	110	$(3.38\pm0.19)E-4$	$(2.49\pm0.08)E-3$	0.809
	2	110	$(3.09\pm0.18)E-4$	$(2.39\pm0.09)E-3$	0.713
	3	110	$(2.98\pm0.17)E-4$	$(2.18\pm0.07)E-3$	0.665

a. Experiment and repetition numbers refer to those in Table 4.4.

Table 5.8. Rate Constants, c_1 and c_2, and Associated 95% Confidence Intervals Determined from eq. (3.5) and Degree of Cure Values, α, less than 50% for Epon 828/mDPA Epoxy, using the Sourour and Kamal (1976) Method.

Exper. No.[a]	Rep. No.[a]	Temp. (°C)	Sourour and Kamal Method	
			c_1 (s^{-1})	c_2 (s^{-1})
2.2	1	60	(1.22 ± 0.49)E-5	(5.04 ± 0.19)E-4
	2	60	(1.52 ± 0.34)E-5	(4.57 ± 0.13)E-4
	3	60	(1.35 ± 0.21)E-5	(4.42 ± 0.08)E-4
2.3	1	70	(2.17 ± 0.61)E-5	(7.93 ± 0.23)E-4
	2	70	(2.15 ± 1.10)E-5	(8.31 ± 0.41)E-4
	3	70	(3.60 ± 1.53)E-5	(7.17 ± 0.59)E-4
2.4	1	100	(1.56 ± 0.31)E-4	(3.22 ± 0.11)E-3
	2	100	(1.58 ± 0.61)E-4	(3.34 ± 0.23)E-3
	3	100	(1.51 ± 0.41)E-4	(2.96 ± 0.15)E-3
2.5	1	110	(2.70 ± 0.37)E-4	(5.16 ± 0.15)E-3
	2	110	(2.83 ± 0.44)E-4	(5.30 ± 0.18)E-3
	3	110	(3.08 ± 0.35)E-4	(4.97 ± 0.14)E-3

a. Experiment and repetition numbers refer to those in Table 4.4.

using linear regression (PLOTit^R, 1989), and they are shown, along with their respective 95% confidence intervals, in Table 5.9.

5.2.2.2 Estimation of the Activation Energy Constants and the Pre-Exponential Factors

Each of the rate constants shown in the kinetic models in eqs. (3.4-3.6) was assumed to follow an Arrhenius relationship with temperature. The activation energy constants and the pre-exponential factors associated with the Arrhenius relationship in eq. (3.7) were estimated using linear regression (PLOTit^R, 1989) from the rate constants, c_1 and c_2, shown in Tables 5.6-5.9. These rate constants are shown along with their associated linear regression curves in Figures 5.10 and 5.11, respectively. Also, the exponential values for m, in Tables 5.6 and 5.7, and n, in Table 5.9, indicated some temperature dependence; this dependence was assumed to linear. Thus, for eq. (3.4),

$$m = m_0 + m_1 T \tag{5.3}$$

and for eq. (3.6),

$$n = n_0 + n_1 T \tag{5.4}$$

where m_0, m_1, n_0, and n_1 are estimated constants using linear regression. The estimated values for the activation energy constants, the pre-exponential factors, and the exponential constants and their respective 95% confidence intervals are compared with values obtained by Sourour and Kamal (1976), Kamal et al. (1973), Ryan and Dutta (1979), and Prime (1970, 1973) for bisphenol-A-diglycidylether (BADGE-DER332)/mPDA systems in Table 5.10. The DER332 BADGE resin has approximately the same structure as the EPON 828 system used here.

In comparing the kinetic parameters estimated in this study with those estimated in the other studies, the parameters characterizing the second rate constant, namely A_2 and E_2, are very similar for the models shown in eqs. (3.4) and (3.5). (It is difficult to

Table 5.9. Rate Constant, c_1, and Exponential, n, and Associated 95% Confidence Intervals Determined from eq. (3.6) and Degree of Cure Values, α, less than 50% for EPON 828/mPDA Epoxy.

Exper. No.[a]	Rep. No.[a]	Temp. (°C)	c_1 (s^{-1})	n
2.2	1	60	$(1.85\pm0.12)E-2$	-1.25 ± 0.18
	2	60	$(1.84\pm0.22)E-2$	-1.11 ± 0.18
	3	60	$(1.49\pm0.14)E-2$	-1.45 ± 0.29
2.3	1	70	$(3.01\pm0.17)E-2$	-1.22 ± 0.17
	2	70	$(3.23\pm0.24)E-2$	-1.12 ± 0.22
	3	70	$(3.32\pm0.35)E-2$	-0.85 ± 0.32
2.4	1	100	0.141 ± 0.023	-1.00 ± 0.46
	2	100	0.161 ± 0.017	-0.84 ± 0.31
	3	100	0.145 ± 0.016	-0.83 ± 0.32
2.5	1	110	0.238 ± 0.023	-0.85 ± 0.29
	2	110	0.254 ± 0.017	-0.79 ± 0.21
	3	110	0.251 ± 0.017	-0.71 ± 0.22

a. Experiment and repetition numbers refer to those in Table 4.4.
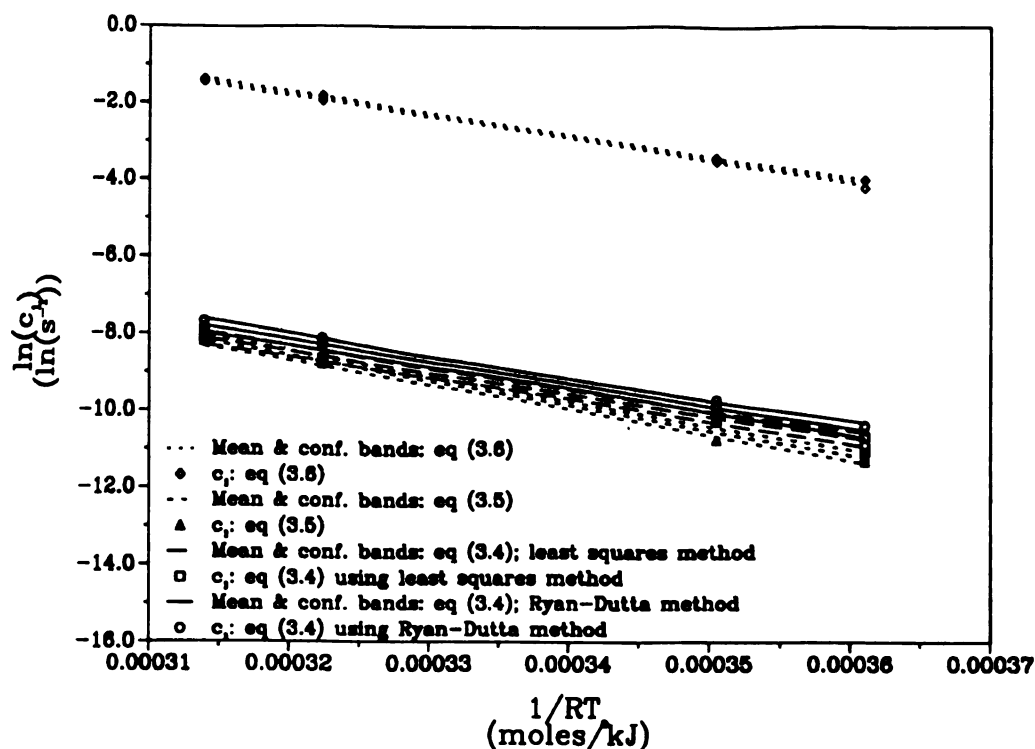
Figure 5.10 Arrhenius Relationship for the First Rate Constant, c_1 in eq. (3.4), (3.5), and (3.6): Ln (c_1) versus $1/RT$ (R = Gas Const. (kJ/mole·K); T_a = Abs. Temp. (°K)).
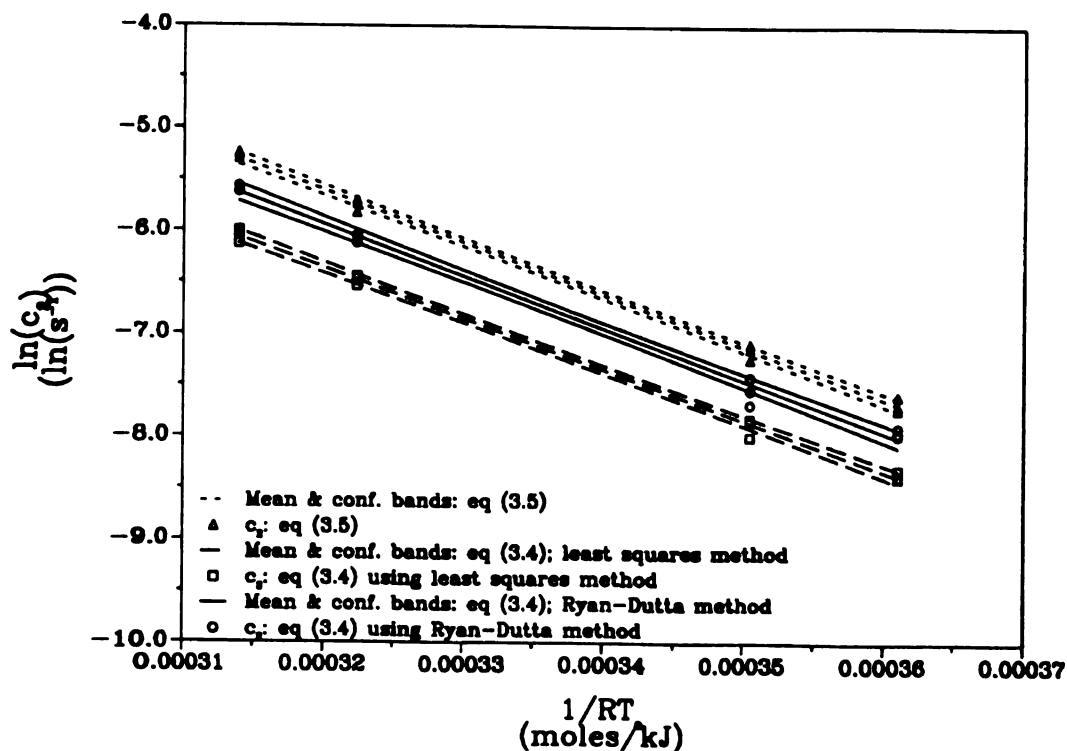
Figure 5.11 Arrhenius Relationship for the Second Rate Constant, c_2 in eq. (3.4), (3.5), and (3.6): Ln (c_2) versus $1/RT$ (R = Gas Const. (kJ/mole·K); T_a = Abs. Temp. (°K)).

Table 5.10. Activation Energy Constants, E_1 and E_2, and Pre-Exponential Factors, A_1 and A_2. Determined from the Arrhenius Relationship (eq. 3.7) and Estimated Rate Constants Estimated from eqs. (3.4), (3.5), and (3.6), for Degree of Cure Values, α, Less than 50% for EPON 828/mPDA Epoxy.

Model	DSC Exp. (temp., °C)	Ea_1 (kJ/mole)	Ea_2 (kJ/mole)	$\ln(A_1)$ $\ln(s^{-1})$	$\ln(A_2)$ $\ln(s^{-1})$	Exponential Constants	Reference (Method)
(3.4)	Isothermal (60-110)	57.4±6.3	50.4±2.9	10.2±2.1	10.2±0.9	$m = m_0+m_1 T$ $m_0 =0.98±0.13$ $m_1 =-(2.0±1.5)E-3$	this study (Ryan and Dutta, 1979, Method)
(3.4)	Isothermal (60-110)	55.8±5.8	49.2±2.1	9.4±2.0	9.4±0.7	$m = m_0+m_1 T$ $m_0 =0.98±0.13$ $m_1 =-(2.3±1.5)E-3$	this study (least squares method)
(3.4)	Isothermal (70-140)	62	48	10.6	9.1	$m = 1$	Kamal et al. (1973)
(3.4)	Isothermal (90-170)	65	46	11.8	not given	$m = 1.06$	Ryan and Dutta (1979)
(3.5)	Isothermal (60-110)	64.5±4.9	50.6±2.0	12.1±1.7	10.6±0.7		this study (linear regres.)
(3.5)	Isothermal (60-130)	81	48	16.0	9.5		Sourour and Kamal (1976)
(3.6)	Isothermal (60-110)	56.1±4.9		16.2±0.8		$n = n_0+n_1 T$ $n_0 =-1.74±0.36$ $n_1 =(8.7±2.1)E-3$	this study (linear regression)
(3.6)	Dynamic (115-130)	50-63		8-12		$n = 0.9-1.3$ $n_0 =-1.74±0.36$	Prime(1970,1973) (Borchardt and Daniels Method)

a. Model refers to equation numbers.

determine whether or not the parameters are statistically equivalent, since the confidence intervals of the parameters estimated in the previous studies were not given, and calculations of the confidence intervals for the activation energy constants and the pre-exponential factors shown for this study did not include the confidence intervals from the rate constants.) The parameters associated with the first rate constant differ by a wider margin. This is to be expected, however, since the first rate constant represents the initial portion of the cure, which is difficult to measure using the DSC, and therefore it is more susceptible to errors. This is evident by the larger confidence intervals for E_1 and A_1 , compared with E_2 and A_2 . Fortunately, since the second rate constant, c_2 , is approximately one order of magnitude greater than the first rate constant, c_1 , as shown in Tables 5.6-5.9, the first rate constant is only dominant during the initial stages of the cure when the degree of cure rate is small.

5.2.3 Diffusion Controlled Reactions and Parameter Estimation

There have been relatively few studies to characterize the cure of an amine-epoxy resin for diffusion controlled reactions (Section 2.2.3). The model presented by Hawley et al. (1988) and shown in eq. (3.16) was first investigated to simulate the curing of the EPON 828/mPDA resin for degrees of cure greater than 0.5. To check the validity of the model, a natural logarithm was applied to eq. (3.16), and then the equation was rearranged as follows,

$$\ln\left[\frac{d\alpha/dt}{(1-\alpha)}\right] = \ln(c_3) - D\alpha$$

A preliminary analysis indicated that the left hand side of the above equation was highly nonlinear, and so this model was deemed to be inappropriate for this analysis.

The alternate model shown in eq. (3.18) was then used to characterize the curing reaction for α greater than 0.50. This model is similar that shown in eq. (3.16) in that the reaction rate was assumed to follow an exponential decay, however, this model is inherently coupled to the kinetic model used for the degree of cure less than 0.50, in which diffusion was assumed to be negligible through the α_D terms in the equation.

The rate constant, c_3, and the diffusion constant, D, were evaluated from the degree of cure rate at the time the reaction became diffusion controlled, which was assumed to be at $\alpha_D = 0.50$, and the degree of cure and associated degree of cure rate values greater α_D, using the nonlinear parameter estimation scheme discussed in Section 3.2.2. Once again is it noted that the selection of α_D was based on the results of the studies discussed in Section 2.2.3 and on visual observation of plots of the degree of cure rate data versus the degree of cure. The estimated parameters, c_3 and D, are shown, along with their 95% confidence intervals, in Table 5.11 for each isothermal DSC experiment. The rate constant was assumed to follow an Arrhenius relationship with temperature (eq. 3.7) and the diffusion constant was assumed to vary linearly with temperature as follows

$$D = D_0 + D_1 T \tag{5.5}$$

The parameters, E_3, A_3, D_0, and D_1, were estimated using linear regression (PLOTit^R, 1989) from these relationships; the estimated parameters are also shown in Table 5.11.

5.2.4 Selection of Kinetic Parameters for use in the Estimation of Thermal Properties during Curing

In order to estimate the thermal properties during the curing of the carbon/epoxy system discussed in Section 4.3, degree of cure rate values were required throughout the cure cycle, as discussed in Section 3.2. The degree of cure rate was found from one of the three kinetic models characterizing the autocatalyzed reaction discussed in Section 3.2.1, and from the diffusion controlled models presented in Section 3.2.2. The selection of the models was based on the confidence intervals of the estimated rate constants, activation energy constants, and pre-exponential values.

For the parameters estimated assuming an autocatalyzed controlled reaction rate (Tables 5.6-5.8), the rate constants estimated using eq. (3.4) for the kinetic model had the lowest confidence intervals, and from Table 5.10, the confidence intervals of the activation energy constants and the pre-exponential factors estimated using eq. (3.4)

Table 5.11. Rate Constant, c_3, and Diffusion Constant, D, and Associated 95% Confidence Intervals Determined from eq. (3.16) and Degree of Cure Values, α, Greater than 50% for EPON 828/mPDA Epoxy.

Exper. No.[a]	Rep. No.[a]	Temp. (°C)	c_3[b] (s^{-1})	D[b]
	1	60	$(2.33\pm0.10)E-2$	6.51 ± 0.18
2.2	2	60	$(4.47\pm0.17)E-2$	6.55 ± 0.22
	3	60	$(4.94\pm0.29)E-2$	7.42 ± 0.38
	1	70	$(4.19\pm0.18)E-2$	4.76 ± 0.16
2.3	2	70	$(4.03\pm0.25)E-2$	4.89 ± 0.21
	3	70	$(5.57\pm0.57)E-2$	5.71 ± 0.46
	1	100	0.265 ± 0.006	1.87 ± 0.07
2.4	2	100	0.276 ± 0.013	1.68 ± 0.12
	3	100	0.311 ± 0.013	1.52 ± 0.12
	1	110	0.496 ± 0.009	0.94 ± 0.05
2.5	2	110	0.477 ± 0.010	0.96 ± 0.05
	3	110	0.493 ± 0.011	0.97 ± 0.06

Ea_3 (kJ/mole)	$\ln(A_3)$ $\ln(s^{-1})$	Diffusion Constants
56.9 ± 8.5	17.1 ± 2.9	$D = D_0 + D_1 T$ $D_0 = 13.4\pm1.2$ $D_1 = -0.117\pm0.013$

a. Experiment and repetitions numbers refer to those in Table 4.4.

were slightly higher than those found using eq. (3.5). Since eq. (3.4) resulted in the lowest confidence intervals for the estimated rate constants, and since the confidence intervals for the activation energy constants did not incorporate the variability of the rate constants, eq. (3.4) was determined to be the best model for the EPON 828/mPDA system studied here. The parameters estimated using eq. (3.4) with the least squares method were used in the estimation procedure for the thermal properties during curing because it incorporated all of the kinetic DSC data in the analysis, instead of relying on just a few points.

The parameters estimated using the alternate diffusion model (eq. 3.18) presented in Section 3.2.2 were used in the estimation of the thermal properties during the second half of the curing reaction. The degree of cure rates estimated using eq. (3.4) at α_D = 0.50 were included in the procedure. The first model presented in Section 3.2.2 by Hawley et al. (1988) was determined to be inappropriate, as discussed in Section 5.2.3.

The kinetic models used in the estimation of the thermal properties during curing are summarized below.

Degree of cure less than 0.50 (autocatalyzed controlled reaction):

$$\frac{d\alpha}{dt} = (c_1 + c_2 \alpha^m)(1 - \alpha)^n \qquad m + n = 2$$

where
$$c_1 = A_1 \exp(-E_1 /R(T+273.15));$$
$$c_2 = A_2 \exp(-E_2 /R(T+273.15));$$
and,
$$m = m_0 + m_1 T.$$

The estimated parameters are:

E_1 = 55.8 kJ/mole,

E_2 = 49.2 kJ/mole,

A_1 = 1.21×10^4 s^{-1},

A_2 = 1.21×10^4 s^{-1},

m_0 = 0.98,

and,
m_1 = -0.0023.

Degree of cure greater than 0.50 (diffusion controlled reaction):

$$\frac{d\alpha}{dt} = \left(\frac{d\alpha}{dt}\right)_{\alpha=\alpha_D} + c_3 \ (\alpha_D - \alpha) e^{-D(\alpha_D - \alpha)}$$

where $\qquad c_3 = A_3 \ \exp(-E_3 \ /R(T+273.15))$,

$\qquad\qquad\qquad \alpha_D = 0.5$

and $\qquad\qquad D = D_0 + D_1 \ T.$

The estimated parameters are:

$\qquad\qquad E_3 = 56.9 \ \text{kJ/mole},$

$\qquad\qquad A_3 = 2.75 \text{X} 10^7 \ \text{s}^{-1},$

$\qquad\qquad D_0 = 13.4,$

and, $\qquad\qquad D_1 = -0.117.$

These models and associated parameters were incorporated into the computer programs *CURE1D* and *PROP1D_CURE* for the estimation of the thermal properties during curing.

5.3 Estimation of the Thermal Properties of Composite Materials during Curing

The estimation of thermal properties of AS4/EPON 828 composite materials during curing is the focal point of this section. First, an analysis of the estimation procedure through the use of simulated data is given in Section 5.3.1. The second section (5.3.2) is devoted to the analysis of the results for the estimated properties from experimental data. The estimated thermal properties are presented and discussed, and improvements for the experimental apparatus and design are proposed. It is emphasized that this is an introductory investigation into this problem, and that the objective here is to establish the procedures and experimental design for the estimation of thermal properties during curing, rather than to determine specific numerical values.

5.3.1. Analysis of the Estimation Procedure using Simulated Data

The procedure for the estimation of thermal properties during the curing of carbon /epoxy composite materials described in Section 3.3 was first implemented and analyzed using simulated temperature data. This simulated temperature data was generated through the use of the computer program *CURE1D*, described in Section 3.3.1, and the resulting temperatures were used as input for the program *PROP1D_CURE* (Section 3.3.2) for the estimation of the thermal properties. A description of the test cases used in the analysis of the estimation procedure is first given, followed by the results of the estimated thermal properties using the simulated data as input.

5.3.1.1 Description of Test Cases

The computer program, *CURE1D*, was used to generate temperature data as input for the program *PROP1D_CURE*. Several different test cases, involving different input conditions for the program *CURE1D* and added random errors, were used in this analysis. The input conditions for *CURE1D* were designed to simulate one of the heat flux pulses in Exp. 3.2, which corresponds to the second experiment during curing described in Section 4.3. The thermo-kinetic problem defined by these parameters can be mathematically described as

$$\frac{\partial}{\partial x}\left[k(T,\alpha)\frac{\partial T}{\partial x}\right] + \rho H_t\frac{d\alpha}{dt} = \rho c_p(T,\alpha)\frac{\partial T}{\partial t} \qquad 0 \leq x \leq L; \qquad t > 0$$

with the boundary conditions,

$$-k(T,\alpha)\frac{\partial T}{\partial x} = q(t) = \begin{cases} 0 \; ; \; 0 < t \leq t_1 \\ q_o \; ; \; t_1 < t \leq t_2 \qquad x = 0 \\ 0 \; ; \; t_2 < t \leq t_3 \end{cases}$$

$$T = T_L(t) \qquad\qquad\qquad x = L; \qquad t > 0$$

and the initial condition,

$$T = T_0 (x) \qquad\qquad 0 \le x \le L; \qquad t = 0$$

where,

$$\frac{d\alpha}{dt} = (c_1 + c_2 \, \alpha^m)(1 - \alpha)^n \qquad\qquad m + n = 2 \qquad \alpha \le 0.5$$

$$c_1 = A_1 \, \exp(-E_1 /R(T+273.15));$$

$$c_2 = A_2 \, \exp(-E_2 /R(T+273.15));$$

$$m = m_0 + m_1 \, T.$$

with the initial condition,

$$\alpha = 0.0 \qquad\qquad t = 0$$

and for $\alpha > 0$,

$$\frac{d\alpha}{dt} = \left(\frac{d\alpha}{dt}\right)_{\alpha = \alpha_D} + c_3 \, (\alpha_D - \alpha)e^{-D(\alpha_D - \alpha)} \qquad\qquad \alpha > 0.5$$

$$c_3 = A_3 \, \exp(-E_3 /R(T+273.15)),$$

$$D = D_0 + D_1 \, T.$$

with the initial condition,

$$\alpha = \alpha_D \qquad\qquad t = t_{\alpha = \alpha_D}$$

where T is °C.

The kinetic parameters presented in Section 5.4.2 were used in the analysis of the kinetic equations shown above. The total heating time $(t_1 - t_2)$ was set equal to 135

seconds and the input heat flux, q_0, was set equal to 800 W/m² ; these values are consistent with the values used in the experimental procedures. A total time, t_t, of 300 seconds was used in this analysis. Based on the measured thicknesses of the experimental composite samples, the hypothetical composite thickness, L, was taken to be 4.5 mm. All of these parameters mentioned thus far were identical in all of the case tests studied. The temperature boundary condition at x = L, $T_L(t)$, and the initial condition, $T_0(x)$, were both taken to be constant and equal to one another in each test case studied. Two different values were used for these parameters; one set of test cases was evaluated at 75°C and a second set was evaluated at 125°C. The analysis also required the initial degree of cure; in all cases it was assumed that the initial degree of cure was uniformly constant. For the test cases at 75°C, a value of 0.40 was used, and for the test cases at 125°C, a initial degree of cure of 0.80 was used.

Two different conditions were used for the thermal properties, in one instance the properties were taken to be constant, and in the second instance, the properties were taken to vary linearly with both temperature and degree of cure. For the first instance, the constant properties were evaluated at 100°C using the equations shown in Table 5.2:

$$k(T) = 0.742 + 9.02 \times 10^{-4} T;$$
$$\text{for } T = 100°C, \quad k = 0.83 \text{ W/m°C};$$

$$\rho c_p(T) = 1.39 + 4.5 \times 10^{-3} T;$$
$$\text{for } T = 100°C, \rho c_p = 1.84 \text{ MJ/m}^3 \text{ °C}.$$

and for the case were the properties were assumed to vary linearly with temperature and degree of cure, the following hypothetical relationship was assumed:

$$k(T,\alpha) = 0.9 k_0 + k_1 T + 0.1 k_0 \alpha,$$

and,

$$\rho c_p(T,\alpha) = 0.9(\rho c_p)_0 + (\rho c_p)_1 T + 0.10(\rho c_{p_0})\alpha$$

(Note that when α equals 1.0, these equations reduce to those shown in Table 5.2.)

Using the values for k_0, k_1, $(\rho c_p)_0$ and $(\rho c_p)_1$ given in Table 5.2, one obtains

$$k(T,\alpha) = 0.6678 + 9.02 \times 10^{-4} T + 0.0742\alpha, \quad (W/m\,^\circ C) \qquad (5.6)$$

and,

$$\rho c_p (T,\alpha) = 1.251 + 4.5 \times 10^{-3} T + 0.139\alpha. \quad (MJ/m^3\,^\circ C) \qquad (5.7)$$

The program *CURE1D* requires input values for k and ρc_p at two different temperatures and two different degree of cure values for the case where the thermal properties vary linearly with both temperature and degree of cure (see eq. 3.21). Therefore, using eqs. (5.6) and (5.7) with temperature values of 75°C and 100°C, and degree of cure values of 0.4 and 0.8, the input property values for *CURE1D* were as follows:

For thermal conductivity, k, (W/m°C)

k(75,0.4) = 0.765; k(75,0.8) = 0.795;

k(100,0.4) = 0.810; and k(100,0.8) = 0.840.

For density-specific heat, ρc_p, (MJ/m^3 °C)

ρc_p(75,0.4) = 1.644; ρc_p(75,0.8) = 1.700;

ρc_p(100,0.4) = 1.869; ρc_p(100,0.8) = 1.925.

The temperatures were calculated using *CURE1D* and the various input parameters described in this section at the locations for x = 0.0 mm, x = 2.25 mm, x = 3.375, and x = 4.5 mm. Normally distributed random temperature errors (Abramowitz and Stegun, 1970) were added to the results from *CURE1D* prior to use in the parameter estimation program *PROP1D_CURE*. Two thermocouples were simulated at each of the above locations by adding two different sets of normally distributed random errors to the temperatures calculated using *CURE1D*. Three different values for the standard deviations of the temperature errors, σ_T, were used: σ_T = 0.0 (no errors); σ_T = 0.10°C; and, σ_T = 0.25°C.

The input parameters for the test cases used in this analysis are summarized in Table 5.12. A total of eleven different test cases were studied, each with different combinations of initial temperature, thermal property, and standard deviation for temperature errors values. The cases with the standard deviation, σ_T, not equal to zero were repeated six times using a different set of random errors with the same standard deviation for each repetition. The temperature change associated with each case was approximately 5°C, and the degree of cure change was approximately 5%.

5.3.1.2 Results from Test Cases

Each of the test cases shown in Table 5.12 was analyzed using *PROP1D_CURE* for the estimation of thermal conductivity and density-specific heat. In each case, the 95% confidence intervals of the estimated parameters were calculated within the program *PROP1D_CURE* assuming that the errors associated with the temperature measurements are correlated and autoregressive (Beck, 1989). These conditions are typically associated with actual temperature measurements, however, the errors in this case were calculated as normally distributed and independent. The differences between these types of errors can be seen through the comparison of the residuals from actual experiments (see Figure 5.1) and the residuals from the hypothetical cases. The residuals from the hypothetical thermocouples at x = 0., x = 1.125 mm, x = 2.25 mm, and x = 3.375 for one test case with σ_T = 0.25 are shown in Figure 5.12. These errors, unlike those shown in Figure 5.1, are uncorrelated and unbiased, with a constant variance throughout the time period. Despite these differences in the types of errors, the use of hypothetical data in the parameter estimation procedure provides an excellent means of testing and evaluating the process.

The estimated thermal conductivity and density-specific heat values for cases 1.1, 2.1-2.6, and 3.1-3.6, involving an initial temperature of 75°C and constant thermal properties are given in Table 5.13. Similarly, results for cases 4.1, 5.1-5.6, and 6.1-6.6, involving an initial temperature of 125°C and constant thermal properties are given in Table 5.14. The percent errors given in both of these tables represent the differences between calculated properties and the input properties values to *CURE1D*. Since the

Table 5.12. Test Cases for the Estimation of Thermal Conductivity, k, and Density-Specific Heat, ρc_p, from Simulated Data for Composite Materials during Curing.

Case No.	T_L, T_0 [a] (°C)	α [b]	σ_T [c] (°C)	k (W/m°C)	ρc_p (MJ/m³ °C)
1.1	75	0.40	0.00	0.83	1.84
2.1-2.6	75	0.40	0.10	0.83	1.84
3.1-3.6	75	0.40	0.25	0.83	1.84
4.1	125	0.80	0.00	0.83	1.84
5.1-5.6	125	0.80	0.10	0.83	1.84
6.1-6.6	125	0.80	0.25	0.83	1.84
7.1	75	0.40	0.00	linear[c] k	linear[c] ρc_p
8.1-8.6	75	0.40	0.10	linear[c] k	linear[c] ρc_p
9.1-9.6	75	0.40	0.25	linear[c] k	linear[c] ρc_p
10.1	125	0.80	0.00	linear[c] k	linear[c] ρc_p
11.1-11.6	125	0.80	0.10	linear[c] k	linear[c] ρc_p
12.1-12.6	125	0.80	0.25	linear[c] k	linear[c] ρc_p

a.   Temperature boundary condition and initial temperature (constant).

b.   Degree of cure.

c.   Standard deviation of temperature errors.
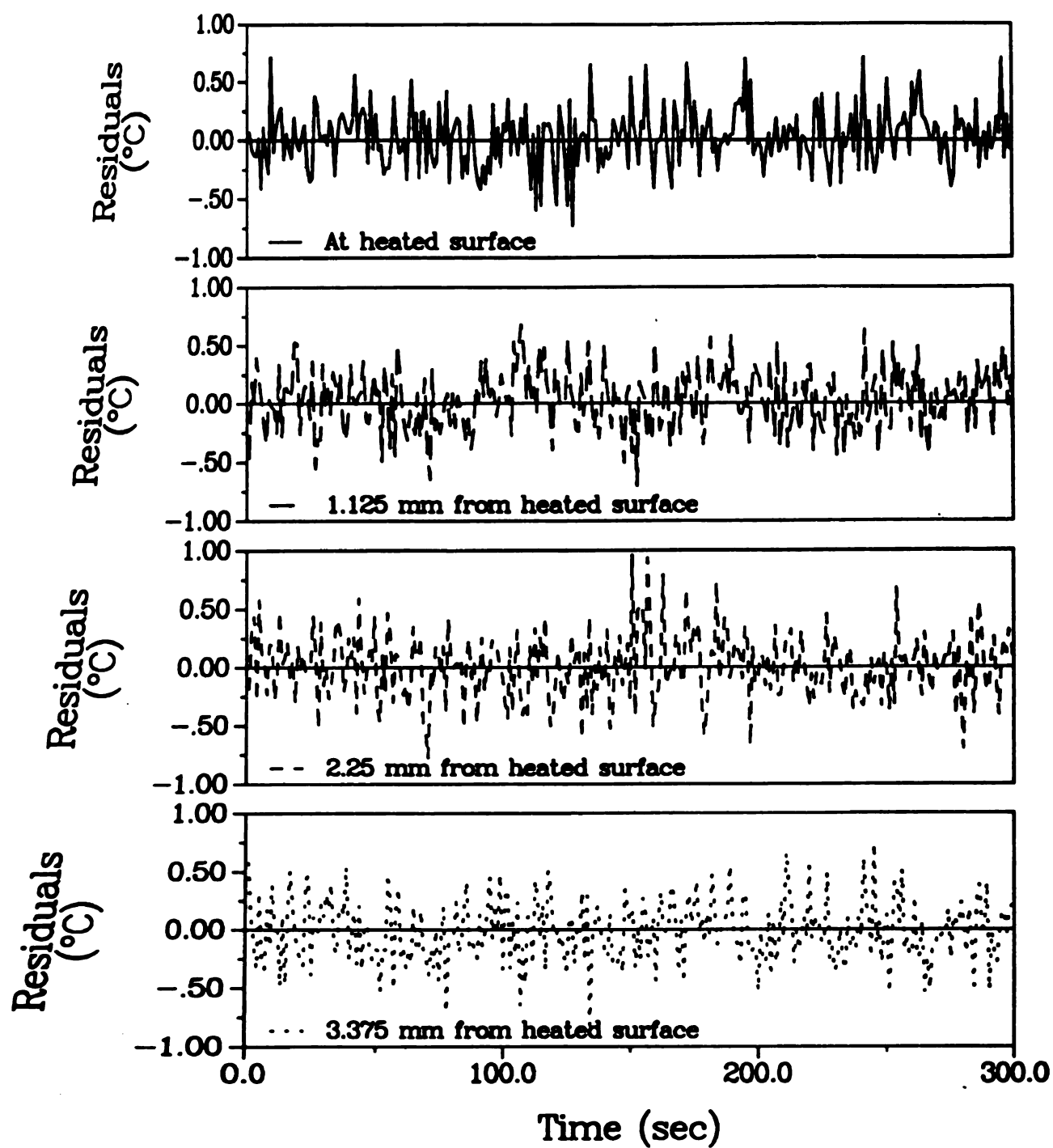
Figure 5.12 Residuals for a Simulated Test Case, using Input Temperature Errors with a Standard Deviation of 0.25°C, at Four Different Locations (total thickness equal to 4.5 mm).

Table 5.13. Estimated Effective Thermal Conductivity, k, Perpendicular to the Fibers and Density-Specific Heat, ρc_p, and the Associated 95% Confidence Intervals for a Simulated Composite with an Initial Temperature of 75°C, an Initial Degree of Cure of 0.40, and Thermal Properties: $k = 0.83$ W/m°C and $\rho c_p = 1.84$ MJ/m³ °C.

Case No.	σ_T^a (°C)	RMS[b] (°C)	Estimated Thermal Conductivity		Estimated Density-Specific Heat	
			k (W/m°C)	Error[c] (%)	ρc_p (MJ/m³ °C)	Error[c] (%)
1.1	0.00	0.003	0.8299	0.01	1.840	0.00
2.1	0.10	0.100	0.8218±0.0063	0.99	1.821±0.034	1.03
2.2	0.10	0.101	0.8315±0.0022	0.18	1.846±0.025	0.60
2.3	0.10	0.098	0.8268±0.0021	0.39	1.865±0.019	1.35
2.4	0.10	0.100	0.8294±0.0021	0.12	1.827±0.039	0.71
2.5	0.10	0.103	0.8291±0.0025	0.11	1.824±0.021	0.87
2.6	0.10	0.101	0.8267±0.0020	0.40	1.852±0.018	0.65
3.1	0.25	0.248	0.8312±0.0051	0.15	1.843±0.045	0.08
3.2	0.25	0.253	0.8217±0.0054	1.00	1.940±0.049	5.44
3.3	0.25	0.248	0.8389±0.0059	1.07	1.841±0.050	0.05
3.4	0.25	0.252	0.8234±0.0056	0.79	1.882±0.049	2.28
3.5	0.25	0.258	0.8373±0.0056	0.70	1.882±0.048	2.28
3.6	0.25	0.256	0.8294±0.0052	0.07	1.820±0.045	1.09

a. *Standard* deviation of temperature errors.
b. *Root mean squared* error between calculated and input temperatures in PROP1D_CURE.
c. **% difference** between input and estimated thermal properties.

Table 5.14. Estimated Effective Thermal Conductivity, k, Perpendicular to the Fibers and Density-Specific Heat, ρc_p, and the Associated 95% Confidence Intervals for a Simulated Composite with an Initial Temperature of 125°C, an Initial Degree of Cure of 0.80, and Thermal Properties: k = 0.83 W/m°C and ρc_p = 1.84 MJ/m³ °C.

Case No.	σ_T[a] (°C)	RMS[b] (°C)	Estimated Thermal Conductivity		Estimated Density-Specific Heat	
			k (W/m°C)	Error[c] (%)	ρc_p (MJ/m³ °C)	Error[c] (%)
4.1	0.00	0.003	0.8296	0.05	1.839	0.05
5.1	0.10	0.100	0.8274±0.0019	0.31	1.808±0.017	1.74
5.2	0.10	0.101	0.8286±0.0019	0.17	1.832±0.017	0.43
5.3	0.10	0.100	0.8297±0.0020	0.04	1.866±0.018	1.41
5.4	0.10	0.100	0.8313±0.0018	0.16	1.847±0.016	0.38
5.5	0.10	0.103	0.8321±0.0018	0.25	1.874±0.016	1.85
5.6	0.10	0.101	0.8309±0.0019	0.11	1.816±0.017	1.30
6.1	0.25	0.251	0.8107±0.0126	2.33	1.801±0.073	2.12
6.2	0.25	0.261	0.8261±0.0043	0.47	1.795±0.039	2.45
6.3	0.25	0.249	0.8336±0.0048	0.43	1.866±0.043	1.41
6.4	0.25	0.250	0.8389±0.0049	1.07	1.880±0.044	2.17
6.5	0.25	0.248	0.8373±0.0044	0.88	1.833±0.039	0.38
6.6	0.25	0.255	0.8357±0.0049	0.69	1.896±0.044	3.04

a. Standard deviation of temperature errors.
b. Root mean squared error between calculated and input temperatures in PROP1D_CURE.
c. % difference between input and estimated thermal properties.

two programs (*CURE1D* and *PROP1D_CURE*) utilize similar numerical methods, the errors associated with the case of $\sigma_T = 0.0$ were very small (<0.05%), as expected, and these errors are assumed to be numerical round-off errors. In all cases, the root mean squared errors (RMS) are close in magnitude to the standard deviation of the input temperature errors, σ_T, as expected. The estimated thermal conductivity values associated with initial temperatures equal to 75°C and 125°C, and σ_T equal to 0.10°C all had errors less than 1% of the input thermal properties used in *CURE1D*. The errors associated with the estimated thermal conductivity values with σ_T equal to 0.25°C were all less than 2.5%. The errors associated with the estimated density-specific heat were typically higher; errors with $\sigma_T = 0.10$°C were less than 2%, while the errors in the estimated density-specific heat values with $\sigma_T = 0.25$°C were less than 2.5%, with the exception of one case for which the error was over 5%. It should be noted that in many cases, the confidence intervals calculated using *PROP1D_CURE* of estimated thermal properties with $\sigma_T > 0.0$°C did not include the thermal properties determined with $\sigma_T = 0.0$°C, as expected.

The results for the cases in which the properties were taken to be linear functions of temperature and degree of cure are given in Table 5.15 for Cases 7.1, 8.1-8.6, and 9.1-9.6, for which the initial temperatures were all equal to 75°C, and in Table 5.16 for Cases 10.1, 11.1-11.6, and 12.1-12.6, in which the initial temperatures are all were equal to 125°C. In these tables, the percent errors given were calculated from the differences between the estimated properties with $\sigma_T = 0.0$ and the estimated properties with $\sigma_T \neq 0.0$. Exact property values were not used in the error analysis in these cases since the properties were assumed to be linear with temperature and degree of cure, and these values varied slightly over each run. However, if the estimated parameters are associated with the average surface temperature over each run and the average degree of cure, one can compare these estimated values with using the same temperature and degree of cure values in eqs. (5.6) and (5.7). The average surface temperatures and degree of cure values were calculated from the cases with $\sigma_T = 0.0$. For the case with an initial temperature of 75°C and initial degree of cure of 0.40,

Table 5.15. Estimated Effective Thermal Conductivity, k, Perpendicular to the Fibers and Density-Specific Heat, ρc_p, and the associated 95% Confidence Intervals for a Simulated Composite with an Initial Temperature of 75°C, an Initial Degree of Cure of 0.40, and Thermal Properties: k (W/m°C) = 0.6678 + 9.03×10^{-4} T + 0.0742α, and ρc_p (MJ/m³ °C) = 1.251 + 0.0045T + 0.139α.

Case No.	σ_T^a (°C)	RMS^b (°C)	Estimated Thermal Conductivity		Estimated Density-Specific Heat	
			k (W/m°C)	$Error^c$ (%)	ρc_p (MJ/m³ °C)	$Error^c$ (%)
7.1	0.00	0.003	0.7678±0.0003	–	1.653±0.002	–
8.1	0.10	0.102	0.7680±0.0019	0.03	1.654±0.016	0.06
8.2	0.10	0.103	0.7663±0.0019	0.20	1.629±0.015	1.45
8.3	0.10	0.100	0.7664±0.0018	0.18	1.668±0.015	0.91
8.4	0.10	0.100	0.7700±0.0019	0.29	1.653±0.015	0.00
8.5	0.10	0.104	0.7697±0.0018	0.25	1.650±0.018	0.18
8.6	0.10	0.098	0.7683±0.0017	0.07	1.657±0.016	0.24
9.1	0.25	0.253	0.7646±0.0050	0.42	1.610±0.042	2.60
9.2	0.25	0.252	0.7652±0.0043	0.34	1.691±0.038	2.30
9.3	0.25	0.255	0.7732±0.0052	0.70	1.706±0.044	3.21
9.4	0.25	0.255	0.7678±0.0047	0.00	1.664±0.041	0.67
9.5	0.25	0.262	0.7672±0.0051	0.08	1.608±0.043	2.72
9.6	0.25	0.251	0.7658±0.0047	0.26	1.649±0.040	0.24

a. Standard deviation of temperature errors.
b. Root mean squared error between calculated and input temperatures in PROP1D_CURE.
c. % difference between test cases with $\sigma_T > 0$ and $\sigma_T = 0$.

Table 5.16.   Estimated Effective Thermal Conductivity, k, Perpendicular to the Fibers and Density-Specific Heat, ρc_p, and the Associated 95% Confidence Intervals for a Simulated Composite with an Initial Temperature of 125°C, an Initial Degree of Cure of 0.80, and Thermal Properties: k (W/m°C) = 0.6678 + 9.03×10^{-4}T + 0.0742α and and ρc_p (MJ/m³ °C) = 1.251 + 0.0045T + 0.139α.

Case No.	σ_T^a (°C)	RMS^b (°C)	Estimated Thermal Conductivity		Estimated Density-Specific Heat	
			k (W/m°C)	$Error^c$ (%)	ρc_p (MJ/m³ °C)	$Error^c$ (%)
10.1	0.00	0.004	0.8443±0.0000	–	1.930±0.000	–
11.1	0.10	0.101	0.8446±0.0009	0.04	1.919±0.017	0.57
11.2	0.10	0.104	0.8442±0.0019	0.01	1.921±0.017	0.47
11.3	0.10	0.100	0.8452±0.0019	1.65	1.948±0.018	0.93
11.4	0.10	0.105	0.8451±0.0021	0.10	1.933±0.019	0.16
11.5	0.10	0.105	0.8469±0.0021	0.31	1.933±0.019	0.16
11.6	0.10	0.099	0.8434±0.0019	0.11	1.938±0.017	0.42
12.1	0.25	0.252	0.8451±0.0051	0.10	1.937±0.046	0.36
12.2	0.25	0.255	0.8479±0.0054	0.43	1.926±0.049	0.21
12.3	0.25	0.250	0.8568±0.0048	1.48	1.962±0.004	1.66
12.4	0.25	0.254	0.8407±0.0055	0.43	1.928±0.051	0.10
12.5	0.25	0.248	0.8436±0.0045	0.08	1.926±0.041	0.21
12.6	0.25	0.259	0.8459±0.0052	0.08	1.972±0.047	2.18

a.   Standard deviation of temperature errors.
b.   Root mean squared error between calculated and input temperatures in PROP1D_CURE.
c.   % difference between test cases with $\sigma_T > 0$ and $\sigma_T = 0$.

$$\overline{T} = 76.8\,^\circ C$$

and, $\quad\overline{\alpha} = 0.425;$

for the case with an initial temperature of 125°C and initial degree of cure of 0.80,

$$\hat{T} = 126.8\,^\circ C$$

and, $\quad\bar{\alpha} = 0.856.$

Substituting the above values into eqs. (5.6) and (5.7), the thermal conductivity and density-specific heat values are:

$$k(76.8,0.425) = 0.7686 \text{ W/m}^\circ C \tag{5.8a}$$

$$\rho c_p(76.8,0.425) = 1.656 \text{ MJ/m}^3\ {}^\circ C \tag{5.8b}$$

$$k(126.8,0.856) = 0.8457 \text{ W/m}^\circ C \tag{5.8c}$$

$$\rho c_p(76.8,0.425) = 1.940 \text{ MJ/m}^3\ {}^\circ C \tag{5.8d}$$

The the parameters estimates resulting from six repetitions in each of the test cases in Tables 5.15 and 5.16 were averaged and compared with the values shown in eqs. (5.8a-d). The average parameter estimates, along with the percent error, based on the difference between these averaged parameter values and those shown in eqs. (5.8a-d) are shown in Table 5.17. In all cases the percent errors are less than 1%, and due to the uncertainty of the temperature and degree of cure values, the estimates from the cases with the lowest variance in the 'measured' temperature values do not necessarily have the lowest percent error.

5.3.2 Analysis of the Estimation of Thermal Properties from Experimental Data

This section involves the analysis of the temperature data from the experiments discussed in Section 4.3 for the estimation of thermal properties during the curing of AS4/EPON 828-mPDA composite samples. The results from this estimation procedure

Table 5.17. Comparison of Averaged Estimated Thermal Conductivity, $\bar{k}$, and Density-Specific Heat, $\overline{\rho c_p}$, Values with Values Calculated Using eqs. (5.6) and (5.7).

Case No.	σ_T^a (°C)	T_L, $T_0^{\ b}$ (°C)	$\bar{k}$ (W/m°C)	Error[c] (%)	$\overline{\rho c_p}$ (MJ/m³ °C)	Error[c] (%)
7.1	0.00	75	0.7678	0.10	1.653	0.16
8.1-8.6	0.10	75	0.7681	0.06	1.652	0.25
9.1-9.6	0.25	75	0.7673	0.17	1.655	0.08
10.1	0.00	125	0.8443	0.17	1.930	0.52
11.1-11.6	0.15	125	0.8449	0.10	1.932	0.41
12.1-12.6	0.25	125	0.8467	0.11	1.942	0.10

a. Standard deviation of temperature errors.

b. Temperature boundary condition and initial temperature (constant).

c. % difference between estimated parameters and parameters calculated using eqs. (5.6) and 5.7).

are first presented in Section 5.3.2.1, followed by analysis of the parameter estimates with regards to errors in Section 5.3.2.2. In the last sub-section, suggestions for improvements in the experimental design are presented.

5.3.2.1 Results from Experimental Data

The thermal properties, effective thermal conductivity perpendicular to the fiber axis and effective density-specific heat, were estimated using the temperature measurements from the three experiments discussed in Section 4.3. The first two of these experiments were conducted during the curing process, and the third experiment was conducted after curing. The third experiment was used as a basis for comparison with the results previously presented for cured composite samples in Section 5.1. The temperature measurements from the first experiment (Exp. 3.1), along with the associated heat flux measurements are shown in Figure 5.13, and temperature measurements from six of the twelve thermocouples in the second experiment (Exp. 3.2) are shown in Figure 5.14. The break in the temperature data at approximately 140 minutes was due to an unexpected abort of the data acquisition program. The calculated temperatures resulting from a simulated experiment, using similar experimental conditions as those used in Exp. 3.2 and thermal properties evaluated at $100\,^{\circ}$C from the results shown in Table 5.1, are shown in Figure 5.15. Exp. 3.2 and 3.3 were conducted using the new Ectron amplifiers and the computer controlled power supply, while Exp. 3.1 was conducted using the Data Translation amplifiers and the manually controlled power supply.

In estimating the thermal properties as functions of temperature and degree of cure, the series of heat flux pulses associated with each experiment were evaluated independently. There were a total of 15 heat flux pulses associated with Exp. 3.1, 16 pulses were associated with Exp. 3.2, and 18 pulses were associated with Exp. 3.3. The average magnitude of the heat flux pulses in Exp. 3.1 was approximately 2000 W/m^2, and the duration time of each of the pulses was 40 seconds. The average magnitudes of the heat flux pulses in Exps. 3.2 and 3.3 were approximately 800 W/m^2 and 1500 W/m^2, respectively, and the duration of each pulse was 135 seconds in both cases.
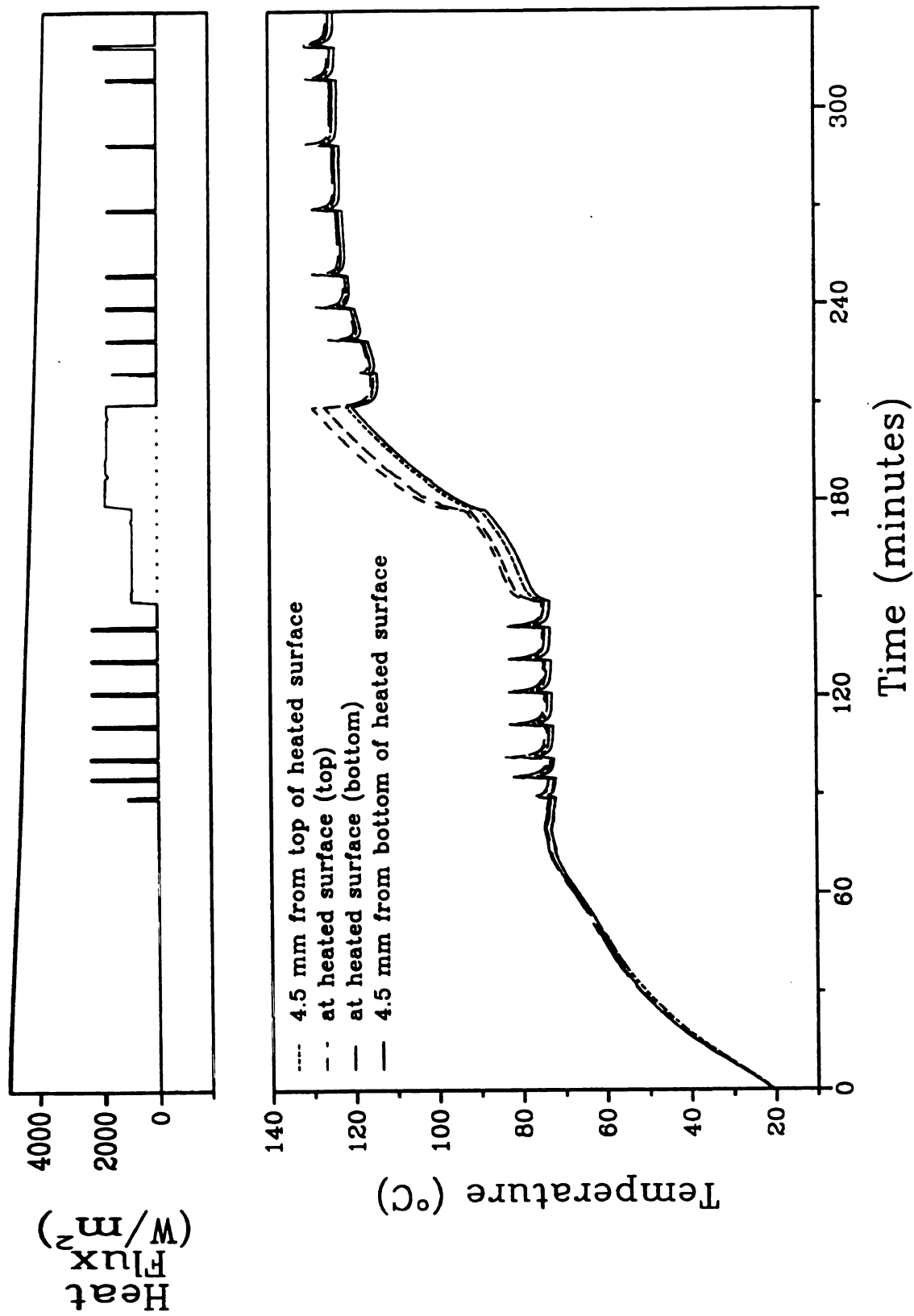
Figure 5.13 Temperature Measurements and Applied Heat Flux from Four Thermocouples in the First Transient Temperature Experiment during Curing (Exp. 3.1).
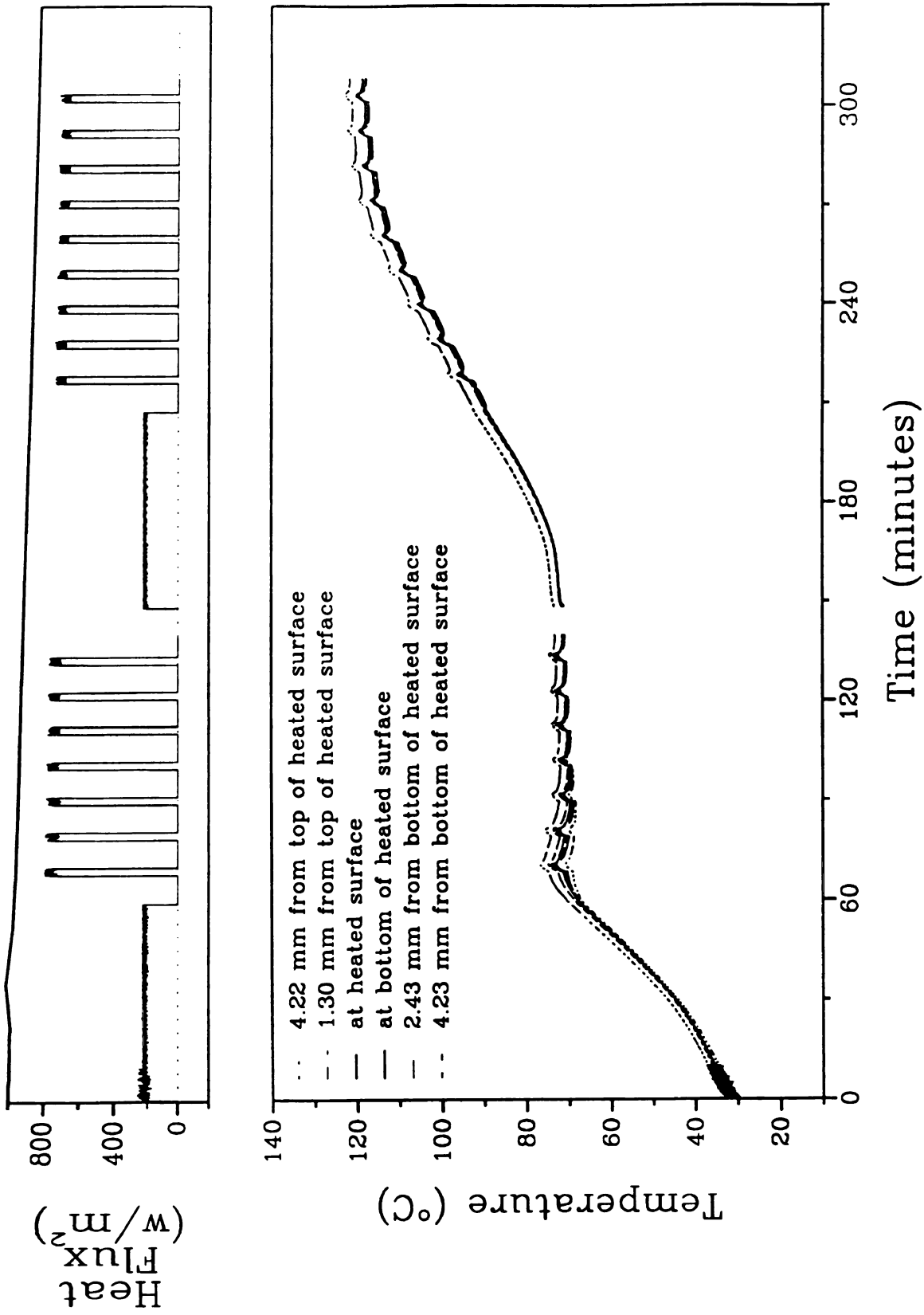
Figure 5.14 Temperature Measurements and Applied Heat Flux from Six Thermocouples in the Second Transient Temperature Experiment during Curing (Exp. 3.2).
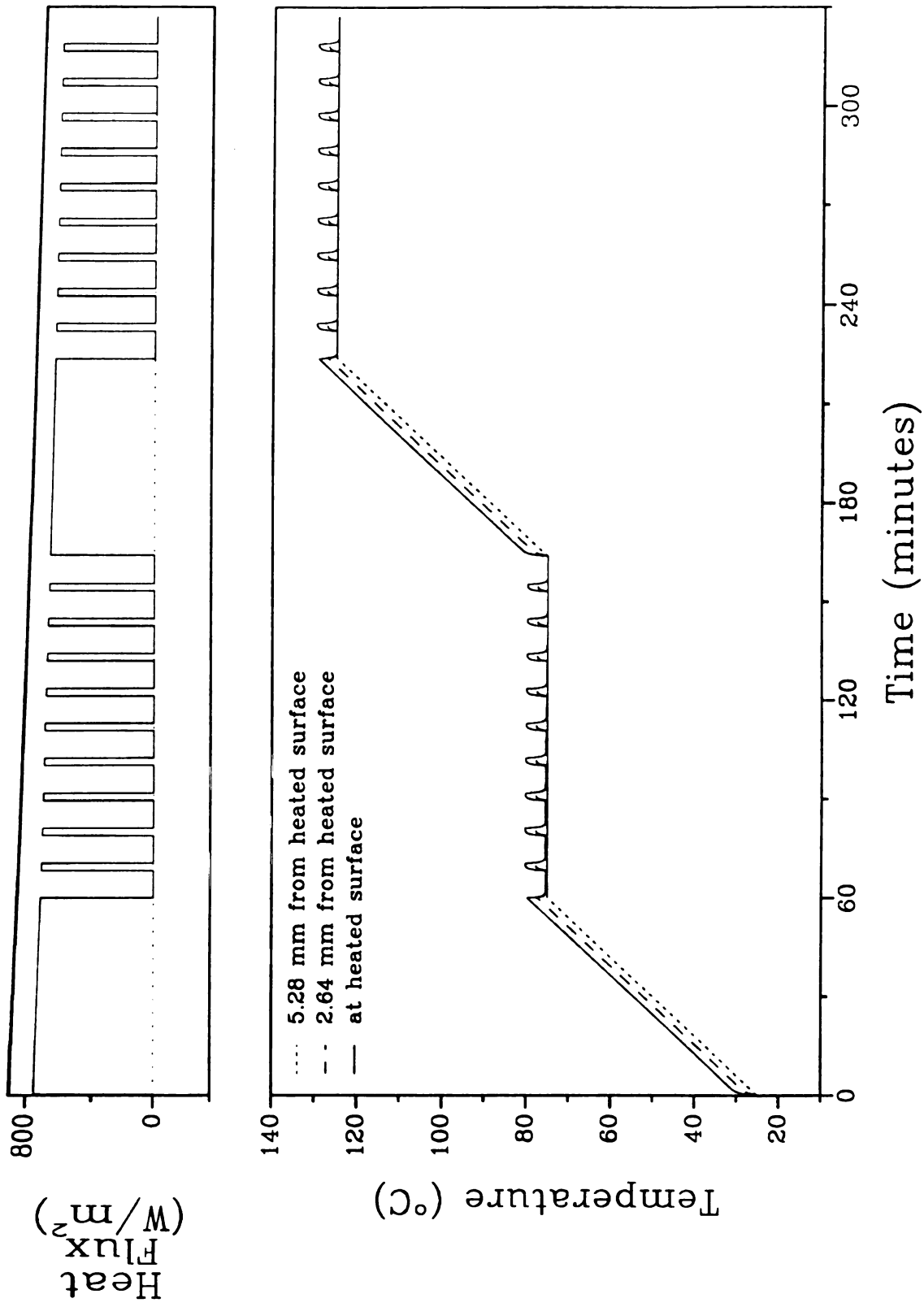
Figure 5.15 Temperatures Resulting from the Simulation of the Second Transient Experiment (3.2) using Thermal Properties Estimated from Cured Composite at 100°C.

Also, the steady state temperatures evident in Figures 5.13 and 5.14 between the heat flux intervals were removed by determining the average temperature from the all of the thermocouple measurements prior to the onset of each heat flux, and subtracting the difference between each thermocouple measurement and the overall average temperature from each thermocouple measurement. Each analysis for the estimation of thermal properties included temperatures from ten seconds prior to the onset of each heat flux interval to at least 150 seconds after the end of each heat flux interval, over which time the thermal properties were assumed constant.

In the experimental design, the heater was placed in the center of the laminate, separating the laminate into two sections, top and bottom, and in using this design, it was assumed that the heat flow was symmetric on either side of the heater. In the estimation of thermal properties, the top and bottom sections were first analyzed separately, assuming half of the measured heat flux was applied to the top section and the other half was applied to the bottom section.

The top and bottom sections associated with the eighteen heat flux pulses in the experiment after curing (Exp. 3.3) were first analyzed for the estimation of the thermal properties, effective thermal conductivity perpendicular to the fiber axis and effective density-specific heat, using *PROP1D_CURE*. The estimated thermal conductivity and density-specific heat values for the top and bottom sections, along with the temperature range over each heat flux pulse and the root mean squared error between the calculated and measured temperatures, are shown in Tables 5.18 and 5.19, respectively. The temperature data from the second experiment during curing (Exp. 3.2) was analyzed in a similar manner, and parameter estimates for the top and bottom sections are given in Tables 5.20 and 5.21, respectively. These tables also include the average degree of cure values at the beginning and end of each analysis interval. In both experiments, during and after curing, the estimated thermal conductivity and density-specific heat values for the bottom section were higher than those estimated for the top section.

The differences in the parameter estimates between the top and bottom sections suggested that, even though the steady state temperatures were subtracted from the data, there was uneven heat flow within the top and bottom sections of the sample. To

Table 5.18. Estimation of Thermal Conductivity, k, Perpendicular to the Fiber Direction and Density-Specific Heat, ρc_p, of Cured AS4/EPON 828-mPDA Composites using Temperature Data from the Top Composite Section Only in Exp. 3.3.

Pulse No.	Temperature Range (°C)	k (W/m°C)	ρc_p (MJ/m³ °C)	RMS[a] (°C)
1	51-57	0.493	0.855	0.147
2	54-60	0.504	0.906	0.142
3	57-63	0.480	0.903	0.168
4	60-65	0.508	0.919	0.153
5	62-68	0.499	0.951	0.153
6	63-69	0.516	0.923	0.143
7	65-70	0.506	0.970	0.148
8	66-71	0.546	0.993	0.149
9	67-71	0.573	0.963	0.219
10	78-84	0.532	1.053	0.180
11	81-86	0.499	0.980	0.220
12	85-91	0.518	1.021	0.149
13	90-96	0.499	1.012	0.187
14	94-100	0.519	1.051	0.164
15	99-105	0.506	1.055	0.211
16	104-110	0.516	1.063	0.160
17	109-114	0.515	1.075	0.167
18	112-117	0.501	1.120	0.182

a. Root mean squared error determined from the differences between calculated and experimental temperatures.

Table 5.19. Estimation of Thermal Conductivity, k, Perpendicular to the Fiber Direction and Density-Specific Heat, ρc_p, of Cured AS4/EPON 828-mPDA Composites using Temperature Data from the Bottom Composite Section Only in Exp. 3.3.

Pulse No.	Temperature Range (°C)	k (W/m°C)	ρc_p (MJ/m^3 °C)	RMS[a] (°C)
1	51-57	1.762	. 1.535	0.136
2	54-60	1.655	1.664	0.139
3	57-63	1.677	1.695	0.127
4	60-65	1.862	1.705	0.151
5	62-68	1.589	2.030	0.176
6	63-69	1.796	1.792	0.138
7	65-70	1.564	1.977	0.144
8	66-71	1.912	1.755	0.155
9	67-71	1.751	1.950	0.171
10	78-84	1.533	1.917	0.160
11	81-86	1.533	1.681	0.163
12	85-91	1.643	1.784	0.156
13	90-96	1.476	1.682	0.137
14	94-100	1.526	1.606	0.144
15	99-105	1.304	1.475	0.157
16	104-110	1.143	1.412	0.175
17	109-114	1.205	1.320	0.167
18	112-117	1.084	1.455	0.178

a. Root mean squared error determined from the differences between calculated and experimental temperatures.

Table 5.20. Estimation of Thermal Conductivity, k, Perpendicular to the Fiber Direction and Density-Specific Heat, ρc_p, of AS4/EPON 828-mPDA Composites during Curing using Temperature Data from the Top Composite Section Only in Exp. 3.2.

Pulse No.	Temperature Range (°C)	Degree of Cure	k (W/m°C)	ρc_p (MJ/m³ °C)	RMS[a] (°C)
1	71-73	0.11-0.15	0.761	1.409	0.161
2	70-72	0.19-0.23	0.806	0.686	0.364
3	70-72	0.27-0.31	0.837	0.702	0.345
4	70-72	0.35-0.39	0.781	0.708	0.287
5	70-73	0.43-0.47	0.870	0.784	0.300
6	70-73	0.51-0.55	0.794	0.720	0.256
7	71-74	0.58-0.62	0.737	0.853	0.195
8	92-96	0.82-0.84	0.590	1.041	0.131
9	97-100	0.85-0.87	0.646	1.122	0.140
10	102-105	0.88-0.90	0.573	1.140	0.116
11	107-110	0.91-0.93	0.564	1.040	0.148
12	111-114	0.94-0.96	0.567	1.119	0.139
13	114-117	0.96-0.98	0.674	1.045	0.114
14	116-118	0.99-1.00	0.661	1.157	0.152
15	116-119	1.00	0.578	1.087	0.119
16	117-120	1.00	0.583	1.166	0.120

a. Root mean squared error determined from the differences between calculated and experimental temperatures.

Table 5.21.   Estimation of Thermal Conductivity, k, Perpendicular to the Fiber Direction and Density-Specific Heat, ρc_p, of AS4/EPON 828-mPDA Composites during Curing using Temperature Data from the Bottom Composite Section Only in Exp. 3.2.

Pulse No.	Temperature Range (°C)	Degree of Cure	k (W/m°C)	ρc_p (MJ/m³ °C)	RMS[a] (°C)
1	71-73	0.11-0.15	5.665	5.168	0.124
2	70-72	0.19-0.23	1.279	2.700	0.104
3	70-72	0.27-0.31	1.533	2.793	0.112
4	70-72	0.35-0.39	1.762	1.515	0.162
5	70-73	0.43-0.47	1.808	2.018	0.116
6	70-73	0.51-0.55	1.786	1.717	0.139
7	71-74	0.58-0.62	1.762	1.762	0.145
8	92-96	0.82-0.84	3.662	2.024	0.143
9	97-100	0.85-0.87	3.205	1.842	0.138
10	102-105	0.88-0.90	3.152	1.590	0.145
11	107-110	0.91-0.93	4.419	1.921	0.143
12	111-114	0.94-0.96	3.651	1.561	0.155
13	114-117	0.96-0.98	3.543	1.721	0.168
14	116-118	0.99-1.00	2.860	1.840	0.147
15	116-119	1.00	2.501	1.453	0.133
16	117-120	1.00	2.845	1.583	0.136

a. Root mean squared error determined from the differences between calculated and experimental temperatures.

eliminate the need for the assumption of symmetrical heat flow, the temperature distributions in the top and bottom sections were averaged. The basis for this averaging can be expressed mathematically as follows:

From eqs. (3.19a-d) and the assumption of constant thermal properties over each analysis interval, the governing equations for the top section can be expressed as,

$$k\frac{\partial}{\partial x}\left(\frac{\partial T_T}{\partial x}\right) + \rho H_t \frac{d\alpha}{dt} = \rho c_p \frac{\partial T_T}{\partial t} \qquad 0 < x < L_T; \quad t > 0 \qquad (5.9a)$$

with the boundary conditions,

$$-k\frac{\partial T_T}{\partial x} = q_T(t) \qquad\qquad x = 0; \qquad t > 0 \qquad (5.9b)$$

$$T = T_{LT}(t) \qquad\qquad x = L_T; \qquad t > 0 \qquad (5.9c)$$

and the initial condition,

$$T = T_o(x) \qquad\qquad 0 \le x \le L_T; \quad t = 0 \qquad (5.9d)$$

where $T_T(x,t)$ represents the temperatures associated with the top section, $q_T(t)$ represents the heat flux boundary condition due to the heater, and L_T is the thickness of the top section.

Likewise, for the bottom section,

$$k\frac{\partial}{\partial x}\left(\frac{\partial T_B}{\partial x}\right) + \rho H_t \frac{d\alpha}{dt} = \rho c_p \frac{\partial T_B}{\partial t} \qquad 0 < x < L_B; \quad t > 0 \qquad (5.10a)$$

with the boundary conditions,

$$-k\frac{\partial T_B}{\partial x} = q_B(t) \qquad\qquad x = 0; \qquad t > 0 \qquad (5.10b)$$

$$T = T_{LB}(t) \qquad\qquad x = L_B; \qquad t > 0 \qquad\qquad (5.10c)$$

and the initial condition,

$$T = T_o(x) \qquad\qquad 0 \le x \le L_B; \quad t = 0 \qquad\qquad (5.10d)$$

where $T_B(x,t)$, $q_B(t)$, and L_B are the temperatures, heat fluxes and thickness associated with the bottom section. By assuming that bottom thicknesses of the top and bottom sections are similar, and substituting the average of these thickness, $L = (L_T + L_B)/2$, for L_T and L_B, eqs. (5.9a) and (5.10a); (5.9b) and (5.10b); (5.9c) and (5.10c); and, (5.9d) and (5.10d) can be added together and averaged as follows:

$$k\frac{\partial}{\partial x}\left(\frac{\partial T}{\partial x}\right) + \rho H_t\frac{d\alpha}{dt} = \rho c_p\frac{\partial T}{\partial t} \qquad 0 < x < L; \qquad\qquad t > 0 \qquad\qquad (5.11a)$$

with the boundary conditions,

$$-k\frac{\partial T}{\partial x} = q(t) \qquad\qquad x = 0; \qquad t > 0 \qquad\qquad (5.11b)$$

$$T = T_L(t) \qquad\qquad x = L; \qquad t > 0 \qquad\qquad (5.11c)$$

and the initial condition,

$$T = T_o(x) \qquad\qquad 0 \le x \le L; \quad t = 0 \qquad\qquad (5.11d)$$

where, $\qquad T = (T_T + T_B)/2$,

$\qquad\qquad\quad T = (q_T + q_B)/2$,

and, $\qquad\quad T = (T_{LT} + T_{LB})/2$

Therefore, the temperature data from both top and bottom sections of the composite can be used by using the average heat flux (which was used when the sections were analyzed separately) for the first boundary condition and the average temperature for the second boundary.

The heat flux intervals in the experiment during curing and the two experiments after curing were then analyzed using temperature measurements from both top and bottom sections. The results for the estimated thermal properties for some of the heat flux pulses in Exp. 3.3, the experiment after curing; Exp. 3.2, the second experiment during curing; and, Exp. 3.1, the first experiment during curing, are shown in Tables 5.22, 5.23, and 5.24, respectively. The 95% confidence intervals shown for these values were determined in the program $PROP1D\_CURE$ (Beck, 1989).

The results from the experiment after curing were first compared with the previous estimates of the thermal properties shown in Table 5.1. All of the estimated thermal conductivity values shown in Table 5.22 were approximately 90% higher than the values at corresponding temperature ranges in Table 5.1, and the density-specific heat values in Table 5.22 were approximately 150% higher than the density-specific heat estimates at corresponding temperature ranges in Table 5.1. In addition, the parameter estimates for both thermal conductivity and density-specific heat indicated no significant temperature dependence, since all of the confidence intervals for each parameter were over lapping. The temperature rises for each heat flux pulse were also compared with the temperature rises for the heat flux pulses resulting from the simulated experiments discussed in Section 5.3.1. The heat fluxes in the simulated experiments were 800 W/m^2, and the resulting temperature rises were approximately 5°C, using thermal properties based on the values shown in Table 5.1. However, the temperature rises shown in Table 5.22 for Exp. 3.3 were only 5°C to 6°C for a heat flux of approximately 1500 W/m^2.

The results from the second experiment during curing (Exp. 3.2) in Table 5.23 were then compared to the results from Exp. 3.3 shown in Table 5.22. As was found for Exp. 3.3, both the estimated thermal conductivity and density-specific heat values in

Table 5.22. Estimation of Thermal Conductivity, k, Perpendicular to the Fiber Direction and Density-Specific Heat, ρc_p, of Cured AS4/EPON 828-mPDA Composites using Temperature Data from Both Top and Bottom Composite Sections in Exp. 3.3.

Pulse No.	Temperature Range (°C)	k (W/m°C)	ρc_p (MJ/m³ °C)	RMS[a] (°C)
2	54-60	1.44±0.10	3.86±0.46	0.330
5	54-60	1.54±0.17	4.25±0.68	0.397
8	66-71	1.47±0.06	3.83±0.31	0.282
11	81-86	1.51±0.14	4.33±0.60	0.340
14	94-100	1.52±0.16	4.47±0.66	0.359
17	109-114	1.56±0.19	4.75±0.79	0.416

a. Root mean squared error determined from the differences between calculated and experimental temperatures.

Table 5.23. Estimation of Thermal Conductivity, k, Perpendicular to the Fiber Direction and Density-Specific Heat, ρc_p, of AS4/EPON 828-mPDA Composites during Curing using Temperature Data from both Top and Bottom Composite Sections in Exp. 3.2.

Pulse No.	Temperature Range (°C)	Degree of Cure	k (W/m°C)	ρc_p (MJ/m³ °C)	RMS[a] (°C)
2	70-72	0.19-0.23	1.67±0.09	3.90±0.56	0.258
4	70-72	0.35-0.39	1.73±0.10	3.80±0.61	0.223
6	70-73	0.51-0.55	1.77±0.08	3.73±0.48	0.205
9	97-100	0.85-0.87	1.65±0.10	4.60±0.57	0.216
12	111-114	0.94-0.96	1.62±0.19	5.24±0.96	0.267
15	116-119	1.00	1.60±0.12	4.62±0.70	0.256

a. Root mean squared error determined from differences between calculated and experimental temperatures.

Table 5.24. Estimation of Thermal Conductivity, k, Perpendicular to the Fiber Direction and Density-Specific Heat, ρc_p, of AS4/EPON 828-mPDA Composites during Curing using Temperature Data from Both Top and Bottom Composite Sections in Exp. 3.1.

Pulse No.	Temperature Range (°C)	Degree of Cure	k (W/m°C)	ρc_p (MJ/m³ °C)	RMS[a] (°C)
2	73-81	0.34-0.38	1.20±0.11	2.60±0.45	0.356
4	74-81	0.49-0.54	1.24±0.20	2.95±0.91	0.415
6	74-81	0.65-0.68	1.24±0.13	2.95±0.60	0.351
9	117-123	0.98-0.99	1.52±0.37	2.50±1.16	0.441
11	121-129	0.99	1.13±0.10	2.71±0.50	0.275
14	123-131	1.00	1.60±0.23	3.40±0.77	0.168

a. Root mean squared error determined from differences between calculated and experimental temperatures.

Table 5.23 are statistically independent of temperature. The estimated thermal conductivity values from Exp. 3.3 were approximately 10% higher than those estimated for Exp. 3.2, and the estimated density-specific heat values were statistically equivalent in both experiments. Also, the temperature rise during this experiment was expected to be on the order of 5°C to 6°C, as discussed in Section 4.3; however, the observed temperature rise was only 2°C to 3°C. This is consistent with the results shown for Exp. 3.3, for which the temperature rise was much less than anticipated.

Finally, the results from the two experiments during curing (Exp. 3.1 and Exp. 3.2) were compared. Both the thermal conductivity and density-specific heat estimates shown in Table 5.23 for Exp. 3.2 were significantly higher than the values shown in Table 5.24 for Exp. 3.1.

Due to the discrepancies between the results from the experiment after curing (Exp. 3.3) and those shown in Table 5.1, the difference in the required heat flux for a given temperature rise between the simulated experiments discussed in Section 5.3.1 and Exp. 3.3, and the differences between the results for the two curing experiments (Exps. 3.1 and 3.2), the parameter estimates from these three experiments were taken to be unreasonable, and additional efforts were concentrated on finding the reasons for the discrepancies listed above with the goal of providing improvements for the experimental design.

5.3.2.2 Investigation of Possible Errors in the Estimation of Thermal Properties during Curing

The residuals, as discussed previously, are useful in gaining insight into possible errors in the experimental design and estimation procedure. The residuals for three of the five thermocouples at the heated surface during the fifth heat flux pulse for Exp. 3.3, conducted after curing, are shown in Figure 5.16. These values are typical of the residuals for all the heat flux pulses in Exp. 3.3. The temperature rise at the heated surface in Exp. 3.3 was approximately 6°C, and the magnitude of the maximum residuals of the three thermocouples shown in this figure were approximately 3.0°C,
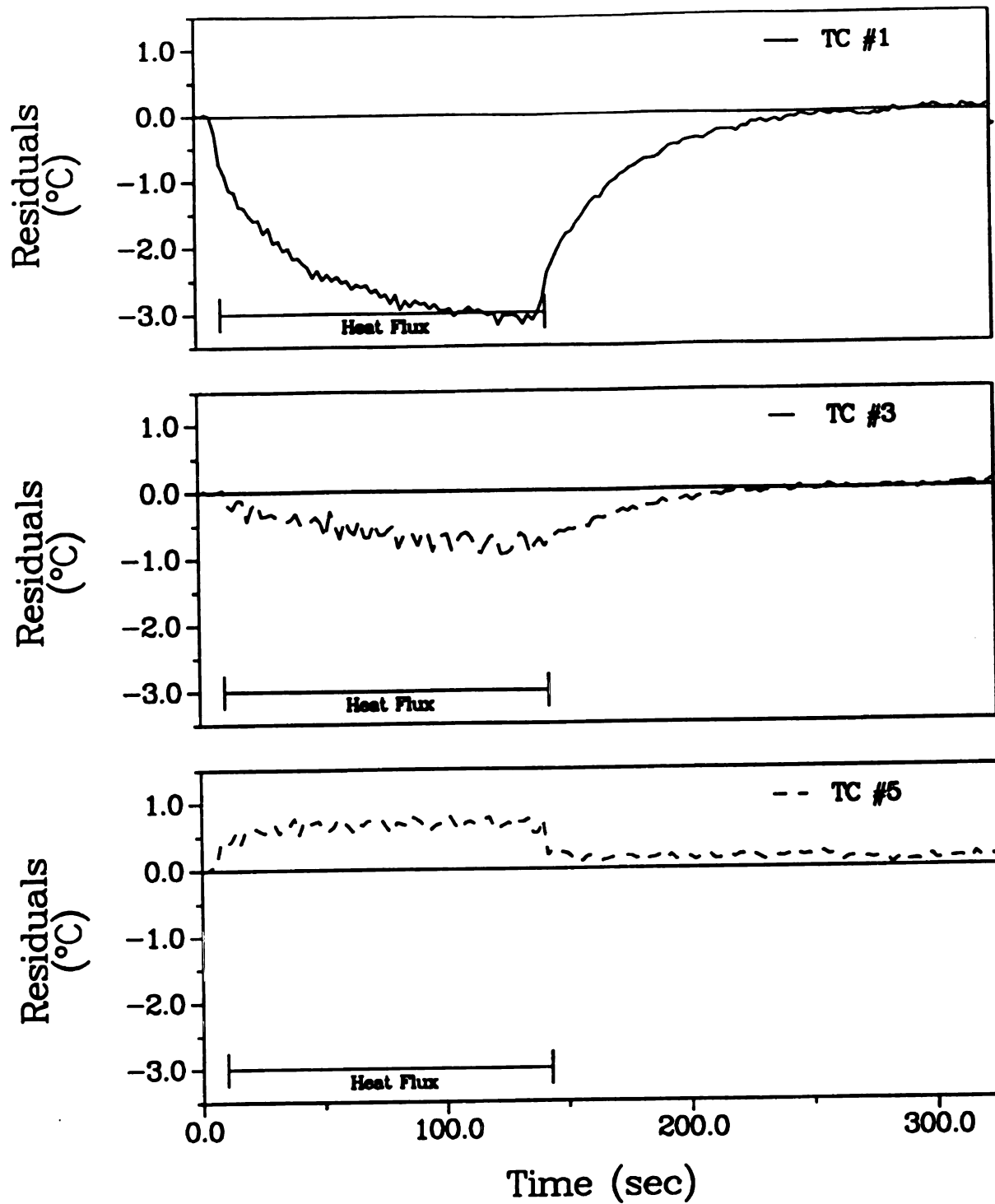
Figure 5.16 Residuals Associated with Three of the Five Thermocouples (TC#1, TC#2, and TC#3) Located at the Heated Surface for the Fifth Heat Flux Pulse in Exp. 3.3.

0.9°C, and 0.8°C, and the magnitude of the maximum residuals for the two thermocouples at the heated surface not shown in this figure were 2.8°C and 1.5°C. These residuals were from 12% to 50% of the maximum temperature rise, which suggests significant errors could be associated with these measurements. The residuals are also very biased, suggesting that the heat flux distribution across the heater was extremely nonuniform; this is especially evident for the first thermocouple.

To further investigate other possible sources of error, the temperatures measurements at the end of the heat flux pulses shown in Tables 5.22, 5.23, and 5.24 were plotted as functions of location with respect to the heated surface in Figures 5.17, 5.18, and 5.19, respectively. The 95% confidence bands shown in each figure were found from the linear regression of temperatures with respect to location using PLOTit^R (1989). In all of these figures, the temperature differences across the composite samples were within the error limits of the thermocouples. This is evident by comparing the confidence bands near the heated surface with the confidence bands of the corresponding regions farthest from the heated surface. In each of the heat flux pulses shown in each figure, the confidence intervals overlapped one another, signifying that the temperatures were statistically equivalent. This also indicated that the temperatures at the boundary away from the heated surface increased, which is illustrated by comparing the measured temperatures farthest from the heated surface in Figures 5.13 and 5.14 with the calculated temperatures farthest from the heat flux boundary condition in the simulated experiment shown in Figure 5.15. The experimental temperatures farthest from the heated surface were shown to increase significantly during the heat flux intervals, while ideally they would remain constant, as shown by the calculated temperatures farthest from the heated surface in Figure 5.15. This suggests that the mechanical press and oven apparatus used in these experiments were inappropriate due to lack of a means to control the temperature at the boundaries of the composite away from the heated surface.

Another point of question is the degree of temperature rise resulting from the applied heat flux. As noted previously, the temperature rises in both Exp. 3.2 and Exp. 3.3 were much less than expected. One possible explanation for this is that the thin
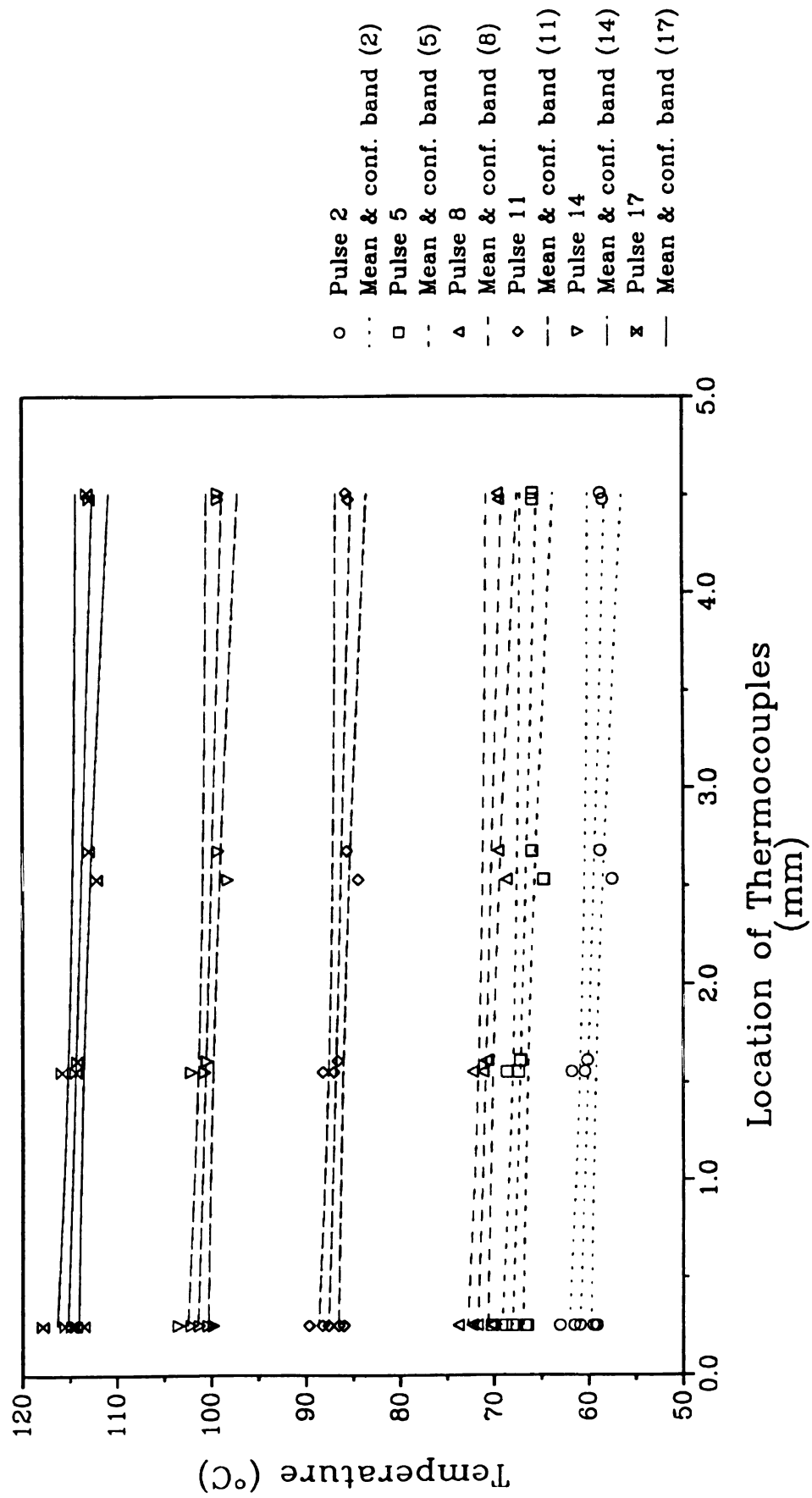
Figure 5.17 Temperature Measurements at the End of the 2nd, 5th, 8th, 11th, 14th, and 17th Heat Flux Pulses in Exp. 3.3 (cured composites) as Functions of Thermocouple Location from the Midsection of the Heater.

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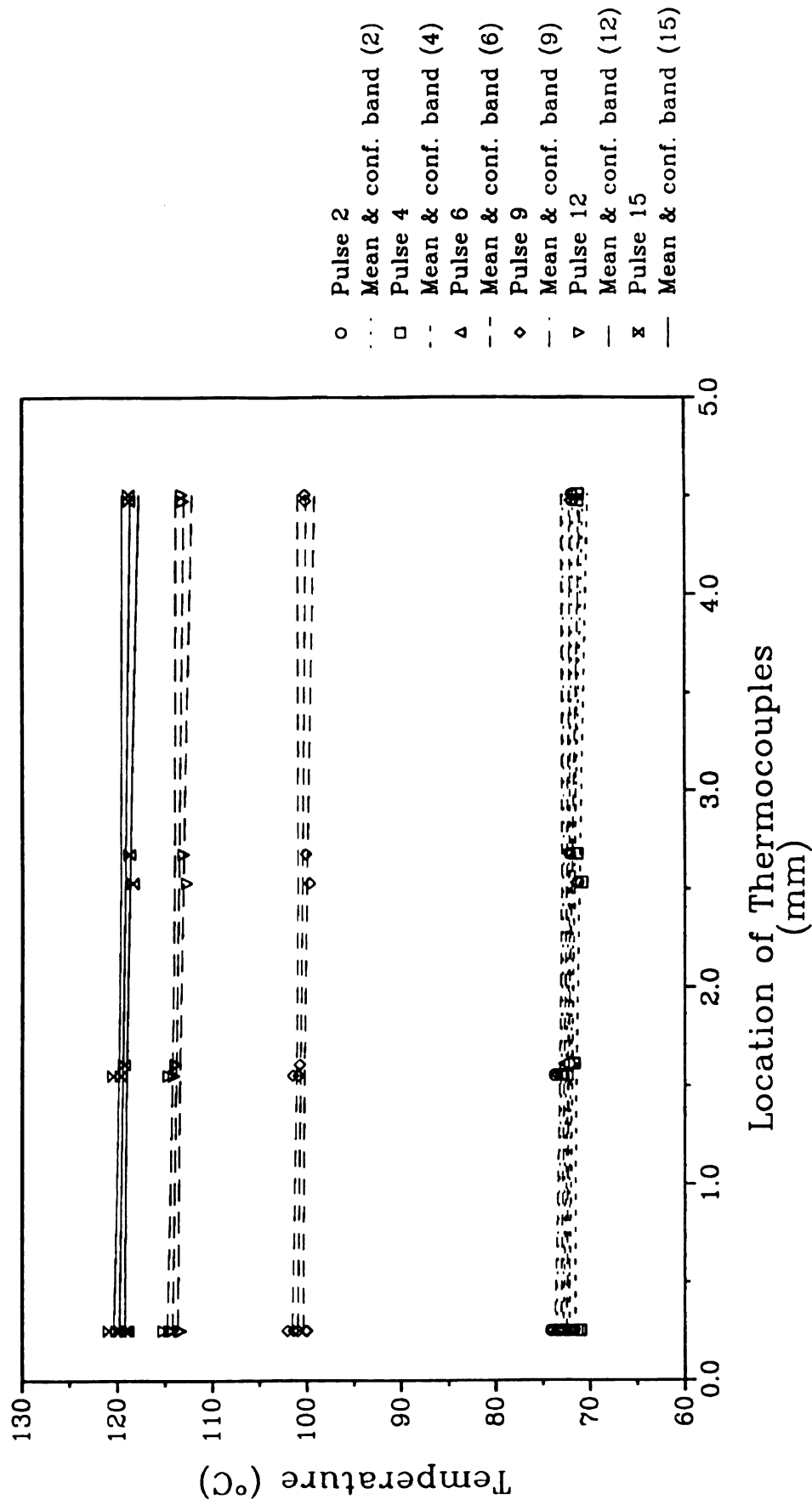
Figure 5.18 Temperature Measurements at the End of the 2nd, 4th, 6th, 9th, 12th, and 15th Heat Flux Pulses in Exp. 3.2 (uncured composites; second experiment) as Functions of Thermocouple Location from the Midsection of the Heater.
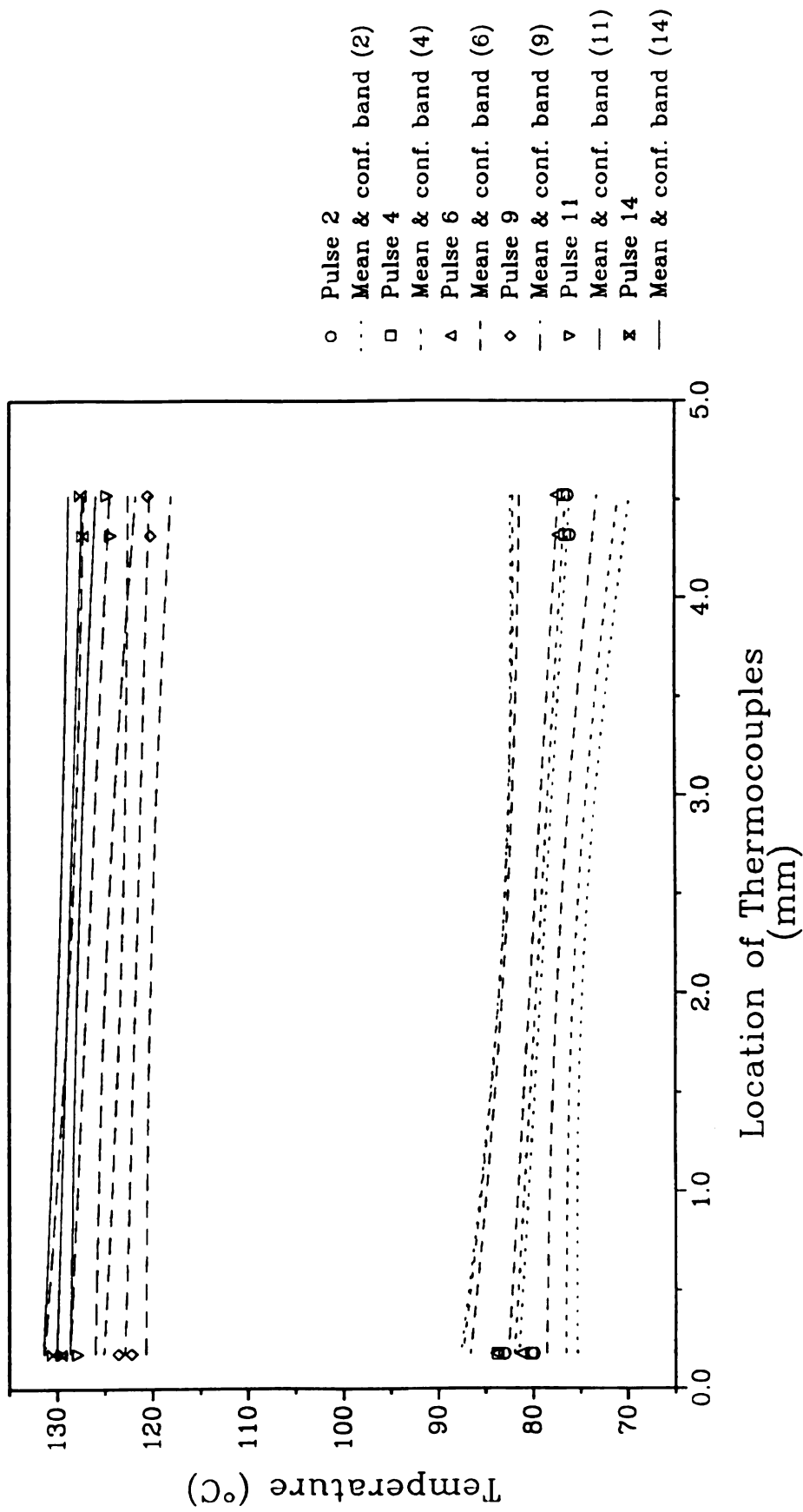
Figure 5.19 Temperature Measurements at the End of the 2nd, 4th, 6th, 9th, 11th, and 14th Heat Flux Pulses in Exp. 3.1 (uncured composites; first experiment) as Functions of Thermocouple Location from the Midsection of the Heater.

sheets of aluminum foil placed on either side of the heater extended past the heater on all sides, acting as a fin around the heater. Due to the low thermal conductivity of the composite compared to that of the heater, it is possible that some of the heat was dissipated through the fin area, reducing the effective heat flux. If the heat flux is calculated using the foil surface area instead of the heater surface area, the resulting heat flux is 65% less than the heat flux calculated from the heater surface area. The cases shown in Table 5.22 for the cured composite were re-evaluated using the adjusted heat flux. The resulting parameter estimates are shown in Table 5.25. Comparing these values to those shown in Table 5.1, the confidence intervals of the density-specific heat values overlapped one another at corresponding temperature levels. The confidence intervals of the thermal conductivity values did not all overlapping, and the results from Exp. 3.3 were approximately 5 - 8% higher than those shown in Table 5.1. However, due to the uncertainties discussed in the previous paragraphs, these estimates were still regarded as unreliable.

5.3.2.3 Improvements in the Experimental Design for the Estimation of Thermal Properties in Composite Materials during Curing

From the investigation of possible sources for error presented in the previous section, several suggestions for improvement in the experimental design are presented.

1. Due to the difficulties of maintaining the proper temperature boundary conditions, it is recommended that the samples be cured in an autoclave or a hydraulic press with heated platens. While the autoclave is generally more effective, the hydraulic press is practically preferred, because the thermocouple wires and the heater connections would not interfere with its operation, while special ports for these wires would be required to use the autoclave. This would also reduce the heating times between room temperature and 75°C, and from 75°C and 125°C. Ideally, the composite would be heated at approximately 2.5°C/minute; however, as shown in Figures 5.13 and 5.14, the samples were heated at a rate less than 1°C/minute.

Table 5.25.   Estimation of Thermal Conductivity, k, Perpendicular to the Fiber Direction and Density-Specific Heat, ρc_p, of Cured AS4/EPON 828-mPDA Composites using Temperature Data from both Top and Bottom Composite Sections in Exp. (3.3), with the Applied Heat Flux Calculated from the Measured Power Input and the Surface Area of the Aluminum Foil Protection Layer.

Pulse No.	Temperature Range (°C)	k (W/m°C)	ρc_p (MJ/m³ °C)	RMS[a] (°C)
2	54-60	0.86±0.02	1.61±0.07	0.144
5	54-60	0.84±0.04	1.71±0.17	0.205
8	66-71	0.90±0.02	1.64±0.07	0.133
11	81-86	0.84±0.04	1.89±0.15	0.195
14	94-100	0.89±0.03	1.82±0.11	0.152
17	109-114	0.88±0.05	1.81±0.18	0.192

a. Root mean squared error determined from the differences between calculated and experimental temperatures.

2. In order to increase the temperature difference across the samples, it is recommended that sample thickness be doubled; this would result in a total thickness of eighty-eight plies, which would require the fabrication of two prepregs for each experiment.

3. Because of the high variations between the thermocouples at the heated surface, it is recommended that a heater with a more uniform heat distribution across the surface be used.

4. In addition, it is recommended that the thermocouples closest to the heated surface be placed one ply away from the heated surface, instead of directly next to the heater.

5. Finally, due to the possible dissipation of heat due to the increased surface area of the foil, the foil should only be applied to the surface area of the heater.

Chapter 6

Summary and Conclusions

The focus of this study was on the estimation of thermal properties for cured carbon/epoxy composites and on the estimation of both thermal and kinetic properties for these composites during curing. Although much attention has been devoted to the determination of the mechanical properties of these materials, relatively little effort has been given to the determination of thermal properties, especially during the curing process.

The first overall objective was related to the estimation of thermal properties of cured carbon/epoxy composites as functions of temperature. Experimental set-ups were designed using AS4/EPON 828 composite samples with the fibers oriented in two different directions: $[0°]_{24}$ and $[0°, \pm30°, \pm60°, 90°]_{2(sym)}$. These experiments were conducted at different initial temperatures ranging from 25°C to 125°C, and the thermal response of the composite to an applied heat flux was measured using thermocouples embedded between composite samples. The thermal conductivity perpendicular to the fiber direction, k, and the density-specific heat, ρc_p, were estimated using an established parameter estimation program, PROP1D (Beck, 1989), which utilizes a Gauss minimization procedure. From this analysis, both k and ρc_p were found as functions of temperature. This analysis differs from previous studies in that the experiments were transient, resulting in the simultaneous estimation of both k and ρc_p, and the properties were estimated as a function of temperature.

The estimation of the kinetic properties associated with the curing of the EPON 828/mPDA epoxy matrix was the second overall objective of this investigation. Isothermal experiments were performed at four different temperatures using differential scanning calorimetry, and the heat of reaction rate was recorded as a function of time. Rate constants were estimated from this data using three different kinetic models for the first half of the curing process, and two different models for the second half of the curing process in which diffusion was assumed to be significant. The kinetic parameters, including activation energy constants and pre-exponential factors, were determined from the estimated rate constants, assuming an Arrhenius relationship with temperature. The most appropriate model was then selected for the first half of the cure, based on the confidence intervals of the estimated kinetic parameters, and a new model was proposed for the diffusion-controlled, second half of the cure cycle.

The last overall objective was related to the estimation of thermal properties as functions of temperature and degree of cure. A new and potentially powerful estimation procedure was proposed for the simultaneous estimation of k and ρc_p throughout the curing process. This procedure was once again based on the minimization of a least squares function. In this case, the parameter estimation program, PROP1D (Beck, 1989), was modified to account for the heat of reaction of the epoxy during curing. This required the solution of an additional differential equation for the kinetic reaction rate in the computations. The estimation procedure was tested and verified using simulated data from the one dimensional curing program, CURE1D, with added normally distributed independent errors. Experiments using AS4/EPON 828 composites, conducted both during and after the curing process, were used in conjunction with the modified parameter estimation program, PROP1D_CURE, for the estimation of thermal properties. Unrealistic estimates of the thermal properties from the experimental data led to the conclusion that the experimental design and equipment used in this study were insufficient for the estimation of the thermal properties. Proposed improvements for the experimental design included curing the samples in a hydraulic press with heated platens and doubling the sample thickness.

The following conclusions were drawn from this study. (All references to thermal conductivity are perpendicular to the fiber axis.)

1.   Both the thermal conductivity and the density-specific heat of cured AS4/EPON 828 composite materials were found to increase with temperature from 25°C to 145°C.

2.   The estimates of the thermal conductivity of AS4/EPON 828 composite samples with an orientation of [0°] were significantly higher than the thermal conductivities estimated for the same material with an orientation of [0°, ±30°, ±60°, 90°], based on a comparison of the estimated linear regression curves given in Table 5.2. For example, at 100°C, the thermal conductivity estimated for the [0°] samples was 7% higher than the thermal conductivity estimated for the [0°, ±30°, ±60°, 90°] samples.

3.   The estimates for thermal conductivity with an orientation of [0°] were within 5% of previously published values (Table 5.4) for the same or similar materials at 25°C.

4.   The thermal history above the glass transition temperature of the epoxy had a significant effect both on the thermal conductivity and density-specific heat of AS4/EPON 828 composite materials; heating a sample for two hours at 150°C increased the thermal conductivity 15% and the density-specific heat 5%, again based on a comparison of the estimated linear regression curves given in Table 5.2 at 100°C.

5.   For the EPON 828/mPDA epoxy system used in this study and degree of cure values less than 50%, the kinetic model used by Ryan and Dutta (1979) was shown to be the most appropriate model of the three kinetic models investigated based on the confidence intervals of the estimated parameters and assuming an autocatalyzed second order reaction.

6.   A new model for the degree of cure rate was presented for degree of cure greater than 50%. In this model, the rate of reaction is assumed to be diffusion-controlled and to follow an exponential decay with the degree of cure.

7.   The procedure for the estimation of the thermal properties during the curing process was verified using the program *PROP1D_CURE* with simulated data plus normally distributed independent errors of 0.25°C (5% of the maximum temperature rise).

The estimated parameters were found to be within 5% of the input parameters used to generate the simulated temperature data.

8. The experimental design and equipment used for the estimation of thermal properties during curing, which included a unheated mechanical press, were not adequate to provide accurate estimates of these parameters. It is recommended that a hydraulic press with heated platens be used in place of the mechanical press and that thicker composite samples be used in the experiments.

9. In the experiments conducted during curing, the thermocouples located at the heated surface had the highest residuals; to reduce these errors it was recommended that these thermocouples be placed at least one ply layer away from the surface of the heater.

APPENDIX A

APPENDIX A

ONE DIMENSIONAL CURING PROGRAM, *CURE1D*

A.1 Summary of Program

The one dimensional curing program, *CURE1D*, discussed in Chapter 3, is presented in this appendix. An outline of the program is given in Table A.1, and a listing of the program, written in Fortran 77 for a VaxstationII/GPX microcomputer is given in Table A.1.

Table A.1 Description of the One Dimensional Curing Program, *CURE1D*.

Subroutine Title	Description
PROGRAM CURE1D	Main program; contains program menu.
SUBROUTINE PROPER	Allows interactive input of thermal properties. Writes data to a file.
SUBROUTINE INPUT1	Allows interactive input of ambient conditions and product geometry. Writes data to a file.
SUBROUTINE INPUT2	Allows interactive input of kinetic properties. Writes data to a file.
SUBROUTINE SOLN	Computes temperature distribution and quality retention as a function of temperature. Calls output subroutine.
SUBROUTINE COEFF	Determines matrix coefficients used in finite difference algorithm.
SUBROUTINE HEAT	Determines heat generation term from kinetic equations.
SUBROUTINE BCFIND	Interpolates boundary conditions.
SUBROUTINE PFIND	Interpolates thermal property values required for the finite difference solution.
SUBROUTINE OUTPUT	Writes input data and resulting temperature and degree of cure values to an output file.

A.2 Program Listing for CURE1D.FOR

```
      PROGRAM CURE1D
c*******************************************************************
c*******************************************************************

c                      One Dimensional

c              Curing Program for Composite Materials

c                              by

c                      Elaine Scott, Ph.D.

c                            1989

c              Copyright (c) 1989 Michigan State University

c                      All rights reserved.

c*******************************************************************

c  Note: this program was adapted from program 'FREEZE1D.FOR', by
c  E.P. Scott, 1987.

c    This program calculates temperature and extent of cure as a
c  function of time and location in composite materials during
c  curing.  It is assumed that one dimensional heat transfer and a
c  second order autocatalyzed chemical reaction occurs with an
c  Arrhenius relationship with temperature.

c    Input parameters include the effective composite density,
c  thermal conductivity, and specific heat.  The kinetic properties,
c  including rate constants and activation energy constants are
c  required to determine the extent of cure.

c    Boundary conditions are assumed to be in the form of a known
c  heat flux or temperature as a function of time.  The initial
c  condition must be a known function of position.

c*******************************************************************

      parameter(maxp=100,maxm=101)

      integer model

      character title*20,ttlfil*4,filyn1*1,filyn2*1,filyn*1,
     &ttlprp*4,ttlkin*4,fildat*12,inpdat*12,kindat*12

      logical itmode

      common/mod/model,/itm/itmode,/ttl/title,ttlfil,ttlprp,ttlkin,
     &/datfil/fildat,inpdat,kindat

C  Set ITMODE = .FALSE. if running batch.
      ITMODE = .TRUE.

      IF(ITMODE)THEN

      write(5,1000)
```

```
1000 format('1',72('*'),/,'0',t21,'One Dimensional Curing Program',
    &/,'0',t35,'by',/,'0',t27,'Elaine Scott, Ph.D.',
    &/,'0',t14,'Copyright (c) 1987 Michigan State',
    &' University',/,' ',t26,'All rights reserved.',/,'0',72('*'))
    WRITE(5,100)
 100 FORMAT('0','Program Menu:',/
    &,/,' ',' 1. Temperature only (no chemical reactions)',
    &/,' ',' 2. Temperature & extent of cure: exact kinetic prop.',
    &/,' ',' 3. Temp. & extent of cure: kinetic prop. with variance',
    &//,' ','Selection?')
    ENDIF
    READ(5,10)model
  10 FORMAT(I1)
    IF(ITMODE)   write(5,200)
 200 format(' ',/,' ','Title: ')
    READ(5,20)TITLE ·
    IF(ITMODE)then
      write(5,300)
 300   format(' ',/,' ','Key word for input boundary conditions ',/
    &  ' ',2x,'and geometry data file; 4 Characters: ')
      READ(5,20)TTLFIL
    endif
    IF(ITMODE)   write(5,320)
 320 format(' ',/,' ','Key word for thermal property data ',
    & 'file; 4 Char.: ')
    READ(5,20)TTLprp
    IF(ITMODE.and.model.ne.1)then
      write(5,340)
 340   format(' ',/,' ','Key word for kinetic property data ',
    &  'file; 4 Char.: ')
      READ(5,20)TTLkin
    endif
  20 FORMAT(A)
    if(itmode) write(5,400)
 400 format(' ',/,' ','Are thermal properties approximations',/,' ',2x,
    &'with temperature stored on file? (y/n) ')
    read(5,20)filyn1
    if(itmode)then
      write(5,500)
 500 format(' ',/,' ','Are input initial and boundary conditions',/,' '
    &  ,2x,'and geometrical dimensions stored on file? (y/n) ')
      read(5,20)filyn2
    endif
    if(model.ne.1) then
      if(itmode) write(5,600)
 600 format(' ',/,' ','Are the kinetic properties stored on file? ',
    &'(y/n) ')
      read(5,20)filyn3
    endif
    if(filyn1.eq.'n'.or.filyn1.eq.'N')then
      call proper
    endif
    if(filyn2.eq.'n'.or.filyn2.eq.'N')then
      call input1
    endif
    if(model.ne.1)then
      if(filyn3.eq.'n'.or.filyn3.eq.'N')then
        call input2
      endif
    endif
    call soln
    end
```

```
c-----------------------------------------------------------------


     SUBROUTINE PROPER


c      This subroutine provides the input for the property functions.
c Input values include effective product thermal conductivities and the
c density-specific heat products at given temperatures and/or extent of
c cure values.

c    Output includes a printout of thermal conductivity and density-
c specific heat products as functions of temperature.

c    The variables used in this subroutine are:

c      Constants-
c      Input Variables-
c            Ntemp - number of temperatures at which properties are given
c            Kp(I) - Effective thermal conductivity (W/mK) at Ith temp.
c            DCp(I) - Density-specific heat product (kJ/m3K) at Ith temp.

c      Misc. Variables-
c            Tc - Temperature for printout.
c            Yn - Character- Y or N


       integer ntemp,prpscr

       double precision dcp(10,10),kp(10,10),tdc(10),tk(10),aldc(10),
      &alk(10)

       character yn*1,title*20,ttlfil*4,ttlprp*4,ttlkin*4,fildat*12,
      &inpdat*12,kindat*12


       logical itmode

       SAVE

       common /ITM/ITMODE,
      &/ttl/title,ttlfil,ttlprp,ttlkin,/datfil/fildat,inpdat,kindat,
      &/mod/model

       IF(.NOT.ITMODE)THEN
            READ(10,*)NTK,NTDC
            IF(MODEL.NE.1)THEN
              READ(10,*)NALK,NALDC
            ELSE
              NALK - 1
              NALDC = 1
            ENDIF
            READ(10,*)(TK(I),I - 1,NTK)
            IF(MODEL.NE.1)THEN
              READ(10,*)(ALK(I),I = 1,NALK)
            ELSE
              ALK(1) = 1.0D0
            ENDIF
            DO I - 1,NTK
              READ(10,*)(KP(I,J),J = 1,NALK)
            ENDDO
            READ(10,*)(TDC(I),I = 1,NTDC)
            IF(MODEL.NE.1)THEN
```

```
            READ(10,*)(ALDC(I),I = 1,NALDC)
          ELSE
            ALDC(1) = 1.0D0
          ENDIF
          DO I = 1,NTDC
            READ(10,*)(DCP(I,J),J = 1,NALDC)
          ENDDO
          GO TO 20
      ENDIF
5     write(5,2000)
2000  format('1',72('-'),/,'0',t27,'Thermal Properties',/,'0',72('-'))
      write(5,600)'Enter number of temperatures for thermal ',
     &'conductivity, k, values:'
  600 format(' ',/,' ',A,A)
      READ(5,*)NTK
      IF(MODEL.NE.1)THEN
        write(5,600)'Enter number of extent of cure values for k:'
  605 format(' ',/,' ',A)
        READ(5,*)NALK
      ELSE
        NALK = 1
      ENDIF
      WRITE(5,610)'Enter temperatures (C) for k (',NTK,') :'
  610 FORMAT(1X,/,1X,A,I2,A)
      READ(5,*)(TK(I),I = 1,NTK)
      IF(MODEL.NE.1)THEN
        WRITE(5,610)'Enter extent of cures for k (',NALK,') :'
        READ(5,*)(ALK(I),I = 1,NALK)
      ELSE
        ALK(1) = 1.0D0
      ENDIF
      WRITE(5,620)'Enter k (W/mC) values: '
  620 FORMAT(1X,/,1X,A,/)
      DO I = 1,NTK
        IF(MODEL.NE.1)THEN
          WRITE(5,630)'Enter k at ',TK(I),'C for ',NALK,
     &      ' extent of cure value(s):'
  630     FORMAT(1X,A,F6.2,A,I2,A)
        ELSE
          WRITE(5,640)'Enter k at ',TK(I),'C :'
  640     FORMAT(1X,A,F6.2,A)
        ENDIF
        READ(5,*)(KP(I,J),J = 1,NALK)
      ENDDO

c End of thermal conductivity input

      WRITE(5,900)
  900 FORMAT(' ',/,' '72('-'),/,' ','Are these values correct? (y/n) ')
      read(5,200)yn
  200 FORMAT(A)
      if(yn.ne.'y'.and.YN.NE.'Y')goto 5

c Start density-specific heat input

6     write(5,600)'Enter number of temperatures for density-',
     &'specific heat, d-Cp, values:'
      READ(5,*)NTDC
      IF(MODEL.NE.1)THEN
        write(5,605)'Enter number of extent of cure values for d-Cp'
        READ(5,*)NALDC
      ELSE
        NALDC = 1
```

```
      ENDIF
      WRITE(5,610)'Enter temperatures (C) for d-Cp (',NTDC,') :'
      READ(5,*)(TDC(I),I = 1,NTDC)
      IF(MODEL.NE.1)THEN
        WRITE(5,610)'Enter extent of cures for d-Cp (',NALDC,') :'
        READ(5,*)(ALDC(I),I = 1,NALDC)
      ELSE
        ALDC(1) = 1.0D0
      ENDIF
      WRITE(5,620)'Enter d-Cp values: '
      DO I = 1,NTDC
        IF(MODEL.NE.1)THEN
          WRITE(5,630)'Enter d-Cp at ',TDC(I),'C for ',NALDC,
     &    ' extent of cure value(s)'
        ELSE
          WRITE(5,640)'Enter d-Cp at ',TDC(I),'C '
        ENDIF
        READ(5,*)(DCP(I,J),J = 1,NALDC)
      ENDDO

        WRITE(5,900)
      read(5,200)yn
      if(yn.ne.'y'.and.YN.NE.'Y')goto 6
   20 CONTINUE


      IF(ITMODE)THEN
        write(6,908)
  908   format(' ',72('-'),//' ','END OF PROPERTY DATA INPUT')
      ENDIF
C
C Convert C temperatures to K temperatures:
C
      DO I = 1,NTK
      TK(I) = TK(I)+273.15D0
      ENDDO
      DO I = 1,NTDC
      TDC(I)= TDC(I)+273.15D0
      ENDDO
C
C Write thermal property data to file
C
      WRITE(FILDAT,1000)TTLPRP,'PRP.DAT'
 1000 FORMAT(' ',A,A)
      OPEN(UNIT=12,NAME=FILDAT(1:12),TYPE='NEW',CARRIAGECONTROL='LIST')
      WRITE(12,*)NTK,NTDC
      WRITE(12,*)NALK,NALDC
      WRITE(12,*)(TK(I),I = 1,NTK)
      WRITE(12,*)(ALK(I),I = 1,NALK)
      DO I = 1,NTK
        WRITE(12,*)(KP(I,J),J = 1,NALK)
      ENDDO
      WRITE(12,*)(TDC(I),I = 1,NTDC)
      WRITE(12,*)(ALDC(I),I = 1,NALDC)
      DO I = 1,NTDC
        WRITE(12,*)(DCP(I,J),J = 1,NALDC)
      ENDDO

      return
      END


C--------------------------------------------------------------------------
```

```
      subroutine input1

c   This subroutine provides the input for the boundary condi-
c tions assuming a known heat flux or temperature at the boundary.
c The boundary conditions may be constant, a linear function of
c time,or a combination of the two.

c   Input varibles include initial temperature, type of boundary
c condition, and time and temperature and/or heat flux at each
c boundary.

      parameter(maxp=100)

      integer Isym,ISTEP,Ishape,m,nbc1,nbc2,ibc1,ibc2

      double precision TI,TQ1(maxp),TQ2(maxp),time1(maxp),
     &time2(maxp),H,L,DZ,DT,PDT

      character yn*1,title*20,ttlfil*4,ttlprp*4,ttlkin*4,fildat*12,
     &inpdat*12,kindat*12

      logical itmode

      common /ttl/title,ttlfil,ttlprp,ttlkin,/mod/model,
     &/itm/itmode,/datfil/fildat,inpdat,kindat

      save

c     IBC1 and IBC2 indicate type of boundary condition at each surface.
c IBC1, IBC2 = 1 indicates temperature boundary condition, and
c IBC1, IBC2 = 2 indicates heat flux boundary condition.
c NTBC1 and NTBC2 indicates the number of temperature and/or heat flux
c values given for each boundary.

      if(itmode)go to 3
      read*,ti,ibc1,nbc1,ibc2,nbc2,ttime,DT,PDT
      do i = 1,nbc1
        read*,time1(i),TQ1(i)
      enddo
      do i = 1,nbc2
        read*,time2(i),TQ2(i)
      enddo
      read Ishape
      if(Ishape.lt.3)then
        read*,l
        h = 1.0d0
      else
        read*,l
        h = 0.0d0
      endif
      go to 500

3     write(5,1)
1 format('1',72('-'),/,'0',27x,'Boundary Conditions',/,'0',72('-'))
5     write(6,10)'Initial product temperature (C): '
10    format(' ',/,' ',A)
      read*,ti
      write(6,20)
20    format(' ',/,' ','Are the boundary conditions symmetrical? ',
     &'(y/n) ',/,' ','(Enter ''y'' for solid cylindrical & spherical ',
     &'geometries) ')
      read(5,2)yn
      if(yn.eq.'y'.or.yn.eq.'Y')Isym = 1
```

```
      write(6,30)
30    format(' ',/,' ','Enter type of boundary condition for IBC1:',
     &/,5x,'1 - temperature boundary,',/,5x,'2 = heat flux boundary')
      read*,Ibc1
      if(Ibc1.eq.1)then
        write(6,15)'Enter number of temperatures given at IBC1 ',
     &'(include values at time = 0, and at time = tmax):'
15    format(/,1x,A,/,1X,A)
        read*,nbc1
      else
        write(6,15)'Enter number of heat fluxes given at IBC1',
     &'(include values at time = 0, and at time = tmax):'
        read*,nbc1
      endif
      if(Isym.ne.1)then
      write(6,32)
32    format(/,1x,'Enter type of boundary condition for IBC2:',
     &/,5x,'1 - temperature boundary,',/,5x,'2 - heat flux boundary')
        read*,Ibc2
        if(Ibc2.eq.1)then
          write(6,15)'Enter number of temperatures given at IBC2 ',
     &    '(include values at time - 0, and at time - tmax):'
          read*,nbc2
        else
          write(6,15)'Enter number of heat fluxes given at IBC2 ',
     &    '(include values at time = 0, and at time = tmax):'
          read*,nbc2
        endif
      endif
      write(6,10)'Enter total time (s):'
      read*,ttime
      write(6,10)'Are these values correct? (y/n) '
      read(5,2)yn
    2 format(a)
      if(yn.ne.'y'.and.yn.ne.'Y')goto 5
      write(6,106)

c input boundary conditions: time and temperature and/or heat flux

100   if(ibc1.eq.1)then
        write(6,10)'Enter time (s) and temperatures (C) for IBC1:'
        do i=1,nbc1
          write(6,120)i
120       format(6X,I2,': ')
          read*,time1(i),TQ1(i)
        enddo
      else
        write(6,10)'Enter time (s) and heat flux (W/m2) for IBC1:'
        do i=1,nbc1
          write(6,120)i
          read*,time1(i),TQ1(i)
        enddo
      endif
      if(ibc2.eq.1)then
        write(6,10)'Enter time (s) and temperatures (C) for IBC2:'
        do i=1,nbc2
          write(6,120)i
          read*,time2(i),TQ2(i)
        enddo
      else
        write(6,10)'Enter time (s) and heat flux (W/m2) for IBC2:'
        do i=1,nbc2
          write(6,120)i
```

```
      read*,time2(i),TQ2(i)
    enddo
  endif

  write(6,10)'Are these values correct? (y/n) '
  read(5,2)yn
  if(yn.ne.'y'.and.yn.ne.'Y')goto 100
  write(6,106)
106   format(' '/,' ',72('-'))

c input geometry and size

140   write(6,150)
150   format('0','Enter product geometry: ',/,' ',5x,'1 = slab',/,' ',5x
    +,'2 = cylinder',/,' ',5x,'3 = sphere')
    read*,Ishape
    if(Ishape.gt.1.and.Isym.eq.0)then
    print*,'Boundary conditions must be symmetrical for cylinder and',
    &' sphere; try again!!'
    go to 3
    endif
    if(Ishape.eq.1)then
      write(6,160)
160   format(' ',/,' ','Enter dimensions for slab:',/,' ',5x,
    &'thickness in direction of heat transfer (m) - ')
      read*,l
      h - 1.0d0
    else
      if(Ishape.eq.2)then
        write(6,180)
180   format(' ',/,' ','Enter dimensions for cylinder:',/,
    +' ',5x,'radius (m)= ')
        read *,l
        h = 1.0d0
      else
        write(6,200)
200   format(' ',/,' ','Enter dimensions for sphere (m):',/,
    +' ',5x,'radius (m)= ')
        read *,l
        h=0.0d0
      endif
    endif
500   ti = ti+273.150d0
    if(Isym.eq.1.and.Ishape.eq.1)L - L*0.50d0
    do i = 1,nbc1
      if(ibc1.eq.1)TQ1(i) - TQ1(i)+273.150d0
      if(Isym.eq.1.or.Ishape.ne.1)then
        if(Ishape.eq.1)then
          TQ2(i) - 0.0d0
          ibc2 - 2
        else
          TQ2(i) = TQ1(i)
          TQ1(i) = 0.0d0
        endif
      endif
    enddo
    do i - 1,nbc1
      if(ibc2.eq.1)TQ2(i) = TQ2(i)+273.150d0
    enddo
    write(6,220)
  220 format(' ',// ',','Enter total number of spatial increments:',/
    &' ',','(Must be a multiple of four.)')
    read*,m
```

```
      ISTEP = m/4
      write(6,230)
  230 format(1x,/,1x,'Enter time step for finite difference ',
     &'calculations:')
      read*,dt
      write(6,240)
  240 format(1x,/,1x,'Enter time step for print out:',/
     &' ','(Must be a multiple of the time step.)')
      read*,pdt

c Check input values

      write(6,10)'Are these values correct? (y/n) '
      read(5,2)yn
      if(yn.ne.'y'.and.yn.ne.'Y')goto 140
      write(6,106)
      write(6,580)
  580 format(' ',//,' ','END OF BOUNDARY CONDITIONS AND GEOMETRY INPUT')

c Write data to file.

  590 write(inpdat,600)ttlfil,'inp.dat'
  600 format(' ',a,a)
      open(unit=12,name=inpdat(1:12),type='new',carriagecontrol='list')
      write(12,700)ibc1,ibc2,nbc1,nbc2,Isym,ti,ttime
  700 format(' ',5(i2,2x),2(2x,E11.5))
      do i = 1,nbc1
        write(12,800)TQ1(i),time1(i)
  800 format(' ',2x,E11.5,2x,f18.2)
      enddo
      do i = 1,nbc2
        write(12,800)TQ2(i),time2(i)
      enddo
      write(12,900)ISHAPE,L,H,M,ISTEP,DT,PDT
  900 format(' ',i1,2(2x,E10.4),2x,i3,2x,i2,2x,E12.5)
      close(unit=12)
      return
      end


c-----------------------------------------------------------------------


      subroutine input2


c     Kinetic properties to determine extent of cure in a composite
c  during curing are entered in this subroutine.  A file titled
c  'TTLFILkin.dat' containing the kinetic properties is created.  This
c  file is reopened in the solution subroutine, so that it may be reused
c  again in subsequent runs.
c
c     The extent of cure is determined assuming an autocatalyzed, second
c  order reaction exists for extent of cure < 0.5, and a diffusion control-
c  led reaction for extent of cure > 0.5.  Nine parameters are required:
c  a) for extent of cure < 0.5; the activation energy constants, EA1 and
c  EA2, the pre-exponential factors, A1 and A2, and the exponent, MEXP;
c  for extent of cure > 0.5; the activation energy constant, EA3, the pre-
c  exponential factor, A3, and the diffusion constant, D3; and for all
c  extent of cure; the density, DENS, and the total heat of reaction, HT.
c  In addition the variances associated with A1, A2, EA1, and EA2 are
c  included in model 3.
```

```
      integer model

      double precision LNA1,LNA2,EA1,EA2,M0,M1,DENS,HT,VA1,VA2,VEA1,
     1         VEA2,LNA3,EA3,D0,D1,D2,A1,A2,A3

      character title*20,ttlfil*4,ttlprp*4,ttlkin*4,fildat*12,
     &inpdat*12,kindat*12

      logical itmode

      common /ttl/title,ttlfil,ttlprp,ttlkin,
     &/mod/model,/itm/itmode,
     &/datfil/fildat,inpdat,kindat

c  Read batch file data (if itmode = .false.)

      if(itmode)go to 1
c
c  Read in values for extent of cure < 0.5
c
      read*,LNA1,LNA2,EA1,EA2,M0,M1
c
c  Read in values for extent of cure < 0.5
c
      read*,LNA3,EA3,D0,D1,D2,DENS,HT
      if(model.eq.3)then
        read*,VA1,VA2,VEA1,VEA2
      endif
      go to 30

c  Read interactive input

    1 write(5,2)
    2 format('1',72('-'),/,'0',t40,'Kinetic Data',/,'0',
     &72('-'))
   10 write(5,100)
  100 format(' ',/,' ','Enter parameters for extent of cure < 0.5 :',/,
     &  ' ',4x,'Pre-exponential factor, LN(A1) LN(1/s) : ')
      read*,LNA1
      write(5,110)'Pre-exponential factor, LN(A2) LN(1/s) : '
  110 format(5x,A)
      read*,LNA2
      write(5,200)'Activation Energy Constant, EA1, (kJ/mole) : '
  200 format(' ',/,5x,A)
      read*,EA1
      write(5,110)'Activation Energy Constant, EA2, (kJ/mole) : '
      read*,EA2
      write(5,200)'Exponent, M = M0 + M1*T(C): '
      WRITE(5,110)'      M0 = '
      read*,M0
      WRITE(5,110)'      M1 = '
      read*,M1
      write(5,210)
  210 format(' ',/,' ','Enter parameters for extent of cure > 0.5 :',/,
     &  ' ',4x,'Pre-exponential factor, LN(A3) LN(1/s) : ')
      read*,LNA3
      write(5,110)'Activation Energy Constant, EA3, (kJ/mole) : '
      read*,EA3
      write(5,200)'Diffusion coefficient, D = D0 + D1*T + D2*T*T (T=C):'
      WRITE(5,110)'      D0 = '
      read*,D0
      WRITE(5,110)'      D1 = '
      read*,D1
```

```fortran
      WRITE(5,110)'      D2 = '
      read*,D2
      write(5,200)'Density (kg/m3) : '
      read*,DENS
      write(5,200)'Total heat of reaction, Ht, (J/kg) : '
      read*,HT
      if(model.eq.3)then
        write(5,200)'Standard deviation of LN(A1) LN(1/s) :'
        read*,VA1
        write(5,110)'Standard deviation of LN(A2) LN(1/s) :'
        read*,VA2
        write(5,200)'Standard deviation of EA1 (kJ/mole) :'
        read*,VEA1
        write(5,110)'Standard deviation of EA2 (kJ/mole) :'
        read*,VEA2
      endif
      write(5,550)
  550 format(' ',/,' ','Are these values correct? (y/n) ')
      read(5,20)yn
   20 format(a)
      if(yn.eq.'n'.or.yn.eq.'N')go to 10

      WRITE(6,560)
  560 FORMAT(' '//,' ','END OF KINETIC DATA INPUT')
   30 A1 = EXP(LNA1)
      A2 = EXP(LNA2)
      A3 = EXP(LNA3)
      EA1 = EA1*1000.0d0
      EA2 = EA2*1000.0d0
      EA3 = EA3*1000.0d0
      if(model.eq.3)then
        vea1 = (vea1*1000.0d0)**2.0d0
        vea2 = (vea2*1000.0d0)**2.0d0
        vA1 = (vA1)**2.0d0
        vA2 = (vA2)**2.0d0
      endif

c Write kinetic data to file.

      write(kindat,600)ttlkin,'kin.dat'
  600 format(' ',a,a)
      open(unit=12,name=kindat(1:12),type='new',carriagecontrol='list')
      write(12,*)A1,A2,EA1
      write(12,*)EA2,M0,M1
      write(12,*)A3,EA3,D0
      write(12,*)D1,D2,DENS
      write(12,*)HT
      if(model.eq.3)then
        write(12,800)VA1,VA2,VEA1,VEA2
  800 format(' ',4(2x,e11.5))
      endif
      close(unit=12)
      return
      end


c ********************************************************************

      SUBROUTINE soln

      parameter(maxm=101,maxp=100,tol=0.10d0,r=8.3140d0)

      IMPLICIT DOUBLE PRECISION(A-H,P-Z)
```

```fortran
      double precision BCTQ(2,2),TAVG,cc(maxm),dd(maxm),a(maxm),
     1       b(maxm),c(maxm),d(maxm),t(maxm,2),pi,pr,AL(MAXM),ALAVG,
     1       ABC(5),AL_5(MAXM),DAL_5(MAXM),TC(12),SIGMA,ALPHA

      character fildat*12,inpdat*12,kindat*12,OUTFIL2*12,OUTFIL3*12

      logical itmode

C Declare variables in common statements

C   Common block /ttl/
      character title*20,ttlfil*4,ttlprp*4,ttlkin*4

C   Common block /kin/
      DOUBLE PRECISION A1,A2,EA1,EA2,M0,M1,DENS,HT,VA1,VA2,VEA1,
     1       VEA2,A3,EA3,D0,D1,D2

C   Common block /prop/
      INTEGER NTDC,NALDC,NTK,NALK
      DOUBLE PRECISION dcp(10,10),tdc(10),aldc(10),kp(10,10),tk(10),
     &alk(10)

C   Common block /bound/
      INTEGER IBC1,IBC2,NBC1,NBC2
      DOUBLE PRECISION TI,TQ1(MAXP),TQ2(MAXP),TIME1(MAXP),TIME2(MAXP)

C   Common block /geom/
      INTEGER ISHAPE,ISYM,M,MP1,ISTEP
      DOUBLE PRECISION H,L,DZ

C   Common block /tim/
      DOUBLE PRECISION DT,TTIME,PDT

c Common blocks.
      common/bound/ibc1,ibc2,nbc1,nbc2,ti,TQ1,TQ2,time1,time2,
     &/ttl/title,ttlfil,ttlprp,ttlkin,
     &/geom/ISHAPE,ISYM,M,MP1,ISTEP,H,L,DZ,
     &/mod/model,/itm/itmode,
     &/datfil/fildat,inpdat,kindat,
     &/prop/dcp,tdc,aldc,kp,tk,alk,ntdc,naldc,ntk,nalk,
     &/KIN/A1,A2,EA1,EA2,M0,M1,DENS,HT,VA1,VA2,VEA1,VEA2,A3,EA3,D0,D1,D2
     &/TIM/TTIME,DT,PDT

      save

c  Read in boundary and initial conditions

      write(inpdat,600)ttlfil,'inp.dat'
  600 format(' ',a,a)
      open(unit=12,name=inpdat(1:12),type='old',carriagecontrol='list')

      read(12,*)ibc1,ibc2,nbc1,nbc2,Isym,ti,ttime
      do i = 1,nbc1
        read(12,*)TQ1(i),time1(i)
      enddo
      do i = 1,nbc2
        read(12,*)TQ2(i),time2(i)
      enddo

C  Input geometry and dimensions

      read(12,*)Ishape,L,h,m,ISTEP,dt,PDT
      close(unit=12)
```

```fortran
c  Read in constant property assumptions

      WRITE(FILDAT,310)TTLprp,'PRP.DAT'
  310 FORMAT(' ',A,A)
      OPEN(UNIT=12,NAME=FILDAT(1:12),TYPE='OLD',CARRIAGECONTROL='LIST')
      READ(12,*)NTK,NTDC
      READ(12,*)NALK,NALDC
      READ(12,*)(TK(I),I = 1,NTK)
      READ(12,*)(ALK(I),I = 1,NALK)
      DO I = 1,NTK
        READ(12,*)(KP(I,J),J = 1,NALK)
      ENDDO
      READ(12,*)(TDC(I),I = 1,NTDC)
      READ(12,*)(ALDC(I),I = 1,NALDC)
      DO I = 1,NTDC
        READ(12,*)(DCP(I,J),J = 1,NALDC)
      ENDDO
      CLOSE(UNIT=12)


c  Read in kinetic data

      if(model.ne.1)then
        write(kindat,600)ttlkin,'kin.dat'
      open(unit=12,name=kindat(1:12),type='old',carriagecontrol='list')
        READ(12,*)A1,A2,EA1
        READ(12,*)EA2,M0,M1
        READ(12,*)A3,EA3,D0
        READ(12,*)D1,D2,DENS
        READ(12,*)HT
        if(model.eq.3)READ(12,*)VA1,VA2,VEA1,VEA2
        close(unit=12)
      endif
C  Read standard deviation for errors added to TC for PROP1D

            WRITE(*,110)'Enter standard deviation (C) for TC errors:'
      READ(*,*)SIGMA

            WRITE(*,110)'Enter seed for random numbers:'
      READ(*,*)IAR


c  Read in initial extent of cure values

      IF(MODEL.NE.1)THEN
        WRITE(*,110)'Enter initial extent of cure (alpha) values:'
110     FORMAT(' ',5X,A)
        WRITE(*,120)'Alpha (constant) = '
120       FORMAT(' ',10X,A)
        READ(*,*)ALPHA
        DO I = 1,M+1
          AL(I) = ALPHA
        ENDDO
      ENDIF

      if(itmode)write(6,1)
    1 format(' ','PROGRAM IS RUNNING!')
      ntime = int(ttime/dt)

      pi = dacos(-1.0d0)
       dz = L/m
      mp1 = m+1


C Initialize temperature
```

```
      DO I = 1,mp1
        DO K = 1,2
          t(I,k)=ti
        enddo
      enddo

      tavg = ti
      time=0.0D0
      BCTQ(1,1) = TQ1(1)
      BCTQ(1,2) = TQ2(1)
      BCTQ(2,1) = TQ1(1)
      BCTQ(2,2) = TQ2(1)

      Ncount=0
      NPR = PDT/DT
      nprint = 0
      IF(MODEL.eq.1)THEN
        HEADTQ=1
      else
        headtq=2
      endif
      call output(nprint,headtq,t,tavg,time,al,alavg,al_5,dal_5,val)
c
c  Write temperatures to file for PROP1DMA.FOR
c
      write(outfil2,1000)ttlfil,'OUT.TEM'
 1000 format(' ',a,a)
      open(unit=13,name=outfil2(1:12),type='new',carriagecontrol='list')
      DO I = 1,5
        ABC(I) = T((I-1)*ISTEP+1,2)
      ENDDO
        WRITE(13,1010)TIME,BCTQ(2,1),t(1,2),t(1,2),t(3,2),t(3,2),
     1        t(5,2),t(5,2),t(7,2),t(7,2),t(9,2),t(9,2)
 1010 FORMAT(1X,F8.2,1X,F10.2,12(1X,F7.2))

      write(outfil3,1000)ttlfil,'OUT.ALP'
      open(unit=14,name=outfil3(1:12),type='new',carriagecontrol='list')
      DO I = 1,5
        ABC(I) = AL((I-1)*ISTEP+1)
      ENDDO
      WRITE(14,1020)TIME,(ABC(I),I=1,5)
 1020 FORMAT(1X,F8.2,5(1X,F7.4))

      j=1

c finite difference solution

      do 160 III=1,ntime

      time = III*dt

c  Find boundary conditions for each time step

      CALL BCFIND(TIME,BCTQ)
c _____

c thomas algorithm

c find coefficients for thomas algorithm

      call coeff(III,BCTQ,T,A,B,C,D,AL,ALAVG,AL_5,DAL_5)

      cc(1)=c(1)/b(1)
```

```
      dd(1)=d(1)/b(1)
      do   k=2,mpl
        kk=k-1
        cc(k)=c(k)/(b(k)-a(k)*cc(kk))
        dd(k)=(d(k)-a(k)*dd(kk))/(b(k)-a(k)*cc(kk))
      enddo
      t(mpl,2)=dd(mpl)
      tavg = t(mpl,2)
      do k=2,mpl
        kk=m-k+2
        t(kk,2)=dd(kk)-cc(kk)*t(kk+1,2)
        tavg = tavg+t(kk,2)
      enddo
      tavg = tavg/mpl

c_____

c find quality distribution and adjust time step

c find mass average quality

c _____
      Ncount=Ncount+1

c printout

      IF(NCOUNT.EQ.NPR)THEN
        nprint = 1
        call output(nprint,headtq,t,tavg,time,al,alavg,al_5,dal_5,val)
        DO I = 1,5
          ABC(I) = T((I-1)*ISTEP+1,2)
        ENDDO
        tc(1)=t(1,2)
        tc(2)=TC(1)
        tc(3)=t(3,2)
        tc(4)=TC(3)
        tc(5)=t(5,2)
        tc(6)=TC(5)
        tc(7)=t(7,2)
        tc(8)=TC(7)
        tc(9)=t(9,2)
        tc(10)=TC(9)
      CALL RANDNU(tc,10,iii,sigma,IAR)
        WRITE(13,1010)TIME,BCTQ(2,1),(TC(I),I = 1,10)
        DO I = 1,5
          ABC(I) = AL((I-1)*ISTEP+1)
        ENDDO
        WRITE(14,1020)TIME,(ABC(I),I=1,5)
        NCOUNT = 0
      ENDIF
c _____

c initial t for next time step

      do 100 i=1,mpl
100   t(i,1)=t(i,2)

c end of finite difference calculations

c ***********************************************************

      BCTQ(1,1) = BCTQ(2,1)
      BCTQ(1,2) = BCTQ(2,2)
```

```
160    continue
       NPRINT=2
       call output(nprint,headtq,t,tavg,time,al,alavg,al_5,dal_5,val)
       close(13)
       CLOSE(14)
       return
       end



c  ********************************************************************


       subroutine coeff(III,BCTQ,T,A,B,C,D,AL,ALAVG,AL_5,DAL_5)

       parameter(maxm=101,maxp=100,r=8.3140d0)

       IMPLICIT DOUBLE PRECISION(A-H,P-Z)

       double precision beta,nu,omega,gama,BCTQ(2,2),aar,ar(maxm),
      &arl(maxm),area,avg1,avg2,da,db,dc,ddd(MAXM),ck(maxm),csd(maxm,2),
      &a(maxm),b(maxm),c(maxm),d(maxm),t(maxm,2),AL(MAXM),
      &DAL(MAXM),ALAVG,pi,dzz,HDEN,AL_5(MAXM),DAL_5(MAXM)


C Declare variables in common statements

C    Common block /kin/

       DOUBLE PRECISION A1,A2,EA1,EA2,M0,M1,DENS,HT,VA1,VA2,VEA1,
       1        VEA2,A3,EA3,D0,D1,D2

C    Common block /prop/

       INTEGER NTDC,NALDC,NTK,NALK
       DOUBLE PRECISION dcp(10,10),tdc(10),aldc(10),kp(10,10),tk(10),
      &alk(10)

C    Common block /bound/

       INTEGER IBC1,IBC2,NBC1,NBC2
       DOUBLE PRECISION TI,TQ1(MAXP),TQ2(MAXP),TIME1(MAXP),TIME2(MAXP)

C    Common block /geom/

       INTEGER ISHAPE,ISYM,M,MP1,ISTEP
       DOUBLE PRECISION H,L,DZ

c    Common block /tim/

       DOUBLE PRECISION TTIME,DT,PDT

       common/bound/ibc1,ibc2,nbc1,nbc2,ti,TQ1,TQ2,time1,time2,
      &/geom/ISHAPE,ISYM,M,MP1,ISTEP,H,L,DZ,
      &/prop/dcp,tdc,aldc,kp,tk,alk,ntdc,naldc,ntk,nalk,
      &/KIN/A1,A2,EA1,EA2,M0,M1,DENS,HT,VA1,VA2,VEA1,VEA2,A3,EA3,D0,D1,D2
      &/MOD/MODEL,
      &/TIM/TTIME,DT,PDT

       pi = dacos(-1.0d0)


c Weighting functions for Crank-Nicolson finite difference method:

c    weighting coefficients for d2T/dz2:
c      for time t:
```

```
      beta=0.50d0
c       for time t+1:
      nu=0.50d0

c    weighting coefficients for dT/dt:
c       for time t:
      omega=-1.0d0
c       for time t+1:
      gama=1.0d0

      dzz=1.0d0/dz
      if(Ishape.eq.2)then
        aar=2.0d0*pi*h
      else
        if(Ishape.eq.3)then
          aar=4.0d0*pi
        endif
      endif


c  Call Subroutine HEAT to determine heat of reaction

      IF(MODEL.NE.1)CALL HEAT(T,AL,DAL,DT,MP1,ALAVG,AL_5,DAL_5)


      do 10 i=1,mp1

c slab

      if(Ishape.eq.1)then
        ar(i)=h
        ar1(i)=h
      else

c cylinder

          if(Ishape.eq.2)then
            ar(i)=aar*(i-1)*dz
            ar1(i)=ar(i)+aar*dz/2.0d0
          else

c sphere

            ar(i)=aar*((i-1)*dz)**2.0d0
            ar1(i)=aar*((i-1)*dz+dz/2.0d0)**2.0d0
          endif
        endif

C Find heat generation term from dalpha/dt:

      HDEN = HT*DENS*DZ
10      continue


      CALL PFIND(T,AL,M,CK,CSD,DT,DZ)

c  **********************************************************

c 1st boundary point

      AVG1 = (AR(1)+AR1(1))*0.50d0
      a(1)=0.0d0
      IF(IBC1.EQ.1)THEN
```

```
      B(1) = 1.0D0
      C(1) = 0.0D0
      D(1) = BCTQ(2,1)
    ENDIF
    IF(IBC1.EQ.2)THEN
      c(1)=nu*dzz*CK(1)*arl(1)
      dc=-beta*dzz*CK(1)*arl(1)

      b(1)=-gama*CSD(1,1)*avg1-c(1)
      db=omega*CSD(1,1)*avg1-dc
      DDD(1)=(-beta*BCTQ(1,1)-nu*BCTQ(2,1)-HDEN*DAL(1)*0.50d0)*ar(1)
      d(1)=db*t(1,1)+dc*t(2,1)+ddd(1)
    ENDIF


c  *********************************************************
c
c  interior points

      do 20 i=2,m
      AVG1 = (AR(I)+AR1(I))*0.50d0
      AVG2 = (AR(I)+AR1(I-1))*0.50d0
      a(I) = nu*dzz*CK(I-1)*arl(i-1)
      da = -beta*dzz*CK(I-1)*arl(i-1)

      c(I) = nu*dzz*CK(I)*arl(i)
      dc = -beta*dzz*CK(I)*arl(i)

      b(I) = -gama*(CSD(I,1)*avg2+CSD(I,2)*avg1)-a(i)-c(i)
      db = omega*(CSD(I,1)*avg2+CSD(I,2)*avg1)-da-dc
      DDD(I) = -HDEN*DAL(I)*ar(I)
      d(I) = da*t(i-1,1)+db*t(i,1)+dc*t(i+1,1)+DDD(I)
20    continue


c  *********************************************************

c  2nd boundary point

      AVG2 = (AR(mp1)+AR1(M))*0.50d0
      c(mp1)=0.0d0

      IF(IBC2.EQ.1)THEN
        A(MP1) = 0.0D0
        B(MP1) = 1.0D0
        D(MP1) = BCTQ(2,2)
      ENDIF
      IF(IBC2.EQ.2)THEN
        a(mp1)=nu*dzz*CK(M)*arl(m)
        da=-beta*dzz*CK(M)*arl(m)

        b(mp1)=-gama*CSD(mp1,2)*avg2-a(mp1)
        db=omega*CSD(mp1,2)*avg2-da
        ddd(MP1)=(-beta*BCTQ(1,2)-nu*BCTQ(2,2)-HDEN*DAL(MP1)*0.5D0)
1            *ar(mp1)
        d(mp1)=da*t(m,1)+db*t(mp1,1)+ddd(MP1)
      ENDIF
      return
      end


c  ***************************************************************

      SUBROUTINE HEAT(T,AL,DAL,DT,MP1,ALAVG,AL_5,DAL_5)

      PARAMETER(MAXM=101,MAXP=100,R=8.314D0)
```

```fortran
      IMPLICIT DOUBLE PRECISION(A-H,P-Z)

      DOUBLE PRECISION AL(MAXM),AL_5(MAXM),ALAVG,C1,C2,C3,D3,DAL(MAXM),
     1      DAL_5(MAXM),DEXP,DT,MEXP,NEXP,SUM,T(MAXM,2),TT

C  Declare variables in common block.

      DOUBLE PRECISION A1,A2,EA1,EA2,M0,M1,DENS,HT,VA1,VA2,VEA1,
     1      VEA2,A3,EA3,D0,D1,D2

      COMMON /KIN/A1,A2,EA1,EA2,M0,M1,DENS,HT,VA1,VA2,VEA1,VEA2,A3,EA3,
     1      D0,D1,D2


C  Extent of cure is found assuming an autocatalyzed second order reaction
C
C  Use Ryan and Dutta method for a < 0.5:
C      da/dt = (c1+c2*a**m)(1-a)**(2-m);
C  where,    c1 = A1exp(-E1/T*R), c2 = A2exp(-E2/T*R), m = m0+m1*(T-273.15)
C
C  Use E. Scott's method for a > 0.5:
C      da/dt = (da/dt)(a=.5) + c3*(0.5-a)exp(-D*(0.5-a))
C  where,    c3 = A3exp(-E3/T*R), D = d0+d1*(T-273.15)
C
      SUM = 0.0D0
      DO 100 J = 1,MP1
C
C  For extent of cure < 0.5:
C
      IF(AL(J).LE.0.50d0)THEN
         MEXP = M0+M1*(T(J,1)-273.15D0)
         NEXP = 2.0D0-MEXP
       C1 = A1*EXP(-EA1/(T(J,1)*R))
       C2 = A2*EXP(-EA2/(T(J,1)*R))
         DAL(J) = (C1+C2*(AL(J)**MEXP))*(1.0D0-AL(J))**NEXP
         AL_5(J) = AL(J)
         DAL_5(J) = DAL(J)
      ELSE
C
C  For extent of cure > 0.5:
C
         AL_5(J) = 0.50D0
           MEXP = M0+M1*(T(J,1)-273.15D0)
           NEXP = 2.0D0-MEXP
         C1 = A1*EXP(-EA1/(T(J,1)*R))
         C2 = A2*EXP(-EA2/(T(J,1)*R))
           DAL_5(J) = (C1+C2*(AL_5(J)**MEXP))*(1.0D0-AL_5(J))**NEXP
         TT = 150.0D0-(T(J,1)-273.15D0)
           DEXP = D0+D1*TT+D2*TT*TT
           IF(DEXP.LT.0.50D0)DEXP = 0.5D0
           DIFAL = AL_5(J)-AL(J)
         C3 = A3*EXP(-EA3/(T(J,1)*R))
           DAL(J) = DAL_5(J)+DIFAL*C3*EXP(-DEXP*DIFAL)/(HT*1D-3)
         IF(DAL(J).LT.0.0D0)DAL(J)=0.0D0
      ENDIF
        AL(J) = AL(J)+DT*DAL(J)
      IF(AL(J).GT.1.0D0)THEN
        AL(J) = 1.0D0
        DAL(J) = 0.0D0
      ENDIF
        SUM = SUM+AL(J)
100   continue
      ALAVG = SUM/MP1
```

```fortran
      RETURN
      END


c  *************************************************************************

      SUBROUTINE BCFIND(TIME,BCTQ)

      PARAMETER(MAXP=100)

      IMPLICIT DOUBLE PRECISION(A-H,P-Z)

      DOUBLE PRECISION TIME,BCTQ(2,2)

C   Common block /bound/
      INTEGER IBC1,IBC2,NBC1,NBC2
      DOUBLE PRECISION TI,TQ1(MAXP),TQ2(MAXP),TIME1(MAXP),TIME2(MAXP)

      common/bound/ibc1,ibc2,nbc1,nbc2,ti,TQ1,TQ2,time1,time2

C  First boundary condition

      DO J = 2,NBC1
        JM1 = J-1
        IF(TIME.LE.TIME1(J))THEN
          BCTQ(2,1) = TQ1(JM1)+(TIME-TIME1(JM1))*(TQ1(J)-TQ1(JM1))/
     &      (TIME1(J)-TIME1(JM1))
          GOTO 10
        ENDIF
        BCTQ(2,1) = TQ1(NBC1-1)+(TIME-TIME1(NBC1-1))*(TQ1(NBC1)-
     &  TQ1(NBC1-1))/(TIME1(NBC1)-TIME1(NBC1-1))
      ENDDO
10    CONTINUE

C  Second boundary condition

      DO J = 2,NBC2
        JM1 = J-1
        IF(TIME.LE.TIME2(J))THEN
          BCTQ(2,2) = TQ2(JM1)+(TIME-TIME2(JM1))*(TQ2(J)-TQ2(JM1))/
     &      (TIME2(J)-TIME2(JM1))
          GOTO 20
        ENDIF
        BCTQ(2,2) = TQ2(NBC2-1)+(TIME-TIME2(NBC2-1))*(TQ2(NBC2)-
     &  TQ2(NBC2-1))/(TIME2(NBC2)-TIME2(NBC2-1))
      ENDDO
20    CONTINUE

      RETURN
      END


c  *************************************************************************



      SUBROUTINE PFIND(T,AL,M,CK,CSPD,DT,DZ)

      PARAMETER (MAXm=101)

      IMPLICIT DOUBLE PRECISION(A-H,P-Z)

      double precision TAVGK,TAVGDC(2),ALAVGK,ALAVGDC(2),CK(MAXM),
     &CSPD(MAXM,2),t(maxm,2),AL(maxm),dt,dz
```

```
C Declare variables in common statements

C   Common block /prop/

      INTEGER NTDC,NALDC,NTK,NALK
      DOUBLE PRECISION dcp(10,10),tdc(10),aldc(10),kp(10,10),tk(10),
     &alk(10),cc

      COMMON /prop/dcp,tdc,aldc,kp,tk,alk,ntdc,naldc,ntk,nalk

C   Common block /MOD/

      INTEGER MODEL

      COMMON /MOD/MODEL

      MP1 = M+1
      cc = 1.0d0*dz/2.0d0

C  Look up table for thermal conductivity

      DO 100 I = 1,MP1
        IF(I.LE.M)THEN
          TAVGK = (T(I,1)+T(I+1,1))*0.50D0
          TAVGDC(1) = 0.75D0*T(I,1)+0.25D0*T(I+1,1)
          IF(MODEL.NE.1)THEN
            ALAVGK = (AL(I)+AL(I+1))*0.50D0
            ALAVGDC(1) = 0.75D0*AL(I)+0.25D0*AL(I+1)
          ENDIF
        ENDIF
        IF(I.GT.1)THEN
          TAVGDC(2) = 0.75D0*T(I,1)+0.25D0*T(I-1,1)
          IF(MODEL.NE.1)THEN
            ALAVGDC(2) = 0.75D0*AL(I)+0.25D0*AL(I-1)
          ENDIF
        ENDIF

C  First find thermal conductivity

C  For MODEL 1, thermal conductivity is a function of temperature only

      IF(MODEL.EQ.1)THEN
      IF(TAVGK.LE.TK(1))THEN
        CK(I)=KP(1,1)+(TAVGK-TK(1))*(KP(2,1)-KP(1,1))/(TK(2)-TK(1))
      ENDIF

      IF(TAVGK.GT.TK(1).AND.TAVGK.LT.TK(NTK))THEN
        DO J = 1,NTK
        IF(J.NE.NTK)THEN
          IF(TAVGK.LE.TK(J+1))THEN
            CK(I)=KP(J,1)+(TAVGK-TK(J))*(KP(J+1,1)-KP(J,1))/
     &        (TK(J+1)-TK(J))
          ENDIF
        ENDIF
        ENDDO
      ENDIF

      IF(TAVGK.GE.TK(NTK))THEN
        CK(I)=KP(NTK,1)+(TAVGK-TK(NTK))*(KP(NTK,1)-KP(NTK-1,1))/
     &    (TK(NTK)-TK(NTK-1))
      ENDIF

      ELSE
```

```
C  For MODEL's 2 and 3, find thermal conductivity as a function of
C  temperature and extent of cure

        IF(NTK.EQ.1.AND.NALK.EQ.1)THEN
          CK(I)=KP(1,1)
          GO TO 105
        ENDIF
        IF(TAVGK.LE.TK(1))THEN
          IF(ALAVGK.LE.ALK(1))THEN
            CK(I)=KP(1,1)+(TAVGK-TK(1))*(KP(2,1)-KP(1,1))/
     &      (TK(2)-TK(1))+(ALAVGK-ALK(1))*(KP(1,2)-KP(1,1))/
     &      (ALK(2)-ALK(1))
          ENDIF
          IF(ALAVGK.GT.ALK(1).AND.ALAVGK.LT.ALK(NALK))THEN
            DO N = 1,NALK
            IF(N.NE.NALK)THEN
              IF(ALAVGK.LE.ALK(N+1))THEN
                CK(I)=KP(1,N)+(TAVGK-TK(1))*(KP(2,N)-KP(1,N))/
     &          (TK(2)-TK(1))+(ALAVGK-ALK(N))*(KP(1,N+1)-KP(1,N))/
     &          (ALK(N+1)-ALK(N))
              ENDIF
            ENDIF
            ENDDO
          ENDIF
          IF(ALAVGK.GE.ALK(NALK))THEN
            CK(I)=KP(1,NALK)+(TAVGK-TK(1))*(KP(2,NALK)-KP(1,NALK))/
     &      (TK(2)-TK(1))+(ALAVGK-ALK(NALK))*(KP(1,NALK)-KP(1,NALK-1))/
     &      (ALK(NALK)-ALK(NALK-1))
          ENDIF
        ENDIF

        IF(TAVGK.GT.TK(1).AND.TAVGK.LT.TK(NTK))THEN
          DO J = 1,NTK
          IF(J.NE.NTK)THEN
            IF(TAVGK.LE.TK(J+1))THEN
              IF(ALAVGK.LE.ALK(1))THEN
                CK(I)=KP(J,1)+(TAVGK-TK(J))*(KP(J+1,1)-KP(J,1))/
     &          (TK(J+1)-TK(J))+(ALAVGK-ALK(1))*(KP(J,2)-KP(J,1))/
     &          (ALK(2)-ALK(1))
              ENDIF
              IF(ALAVGK.GT.ALK(1).AND.ALAVGK.LT.ALK(NALK))THEN
                DO N = 1,NALK
                IF(N.NE.NALK)THEN
                  IF(ALAVGK.LE.ALK(N+1))THEN
                    CK(I)=KP(J,N)+(TAVGK-TK(J))*(KP(J+1,N)-KP(J,N))/
     &              (TK(J+1)-TK(J))+(ALAVGK-ALK(N))*(KP(J,N+1)
     &              -KP(J,N))/(ALK(N+1)-ALK(N))
                  ENDIF
                ENDIF
                ENDDO
              ENDIF
              IF(ALAVGK.GE.ALK(NALK))THEN
                CK(I)=KP(J,NALK)+(TAVGK-TK(J))*(KP(J+1,NALK)
     &          -KP(J,NALK))/(TK(J+1)-TK(J))+(ALAVGK-ALK(NALK))
     &          *(KP(J,NALK)-KP(J,NALK-1))/(ALK(NALK)-ALK(NALK-1))
              ENDIF
            ENDIF
          ENDIF
          ENDDO
        ENDIF

        IF(TAVGK.GE.TK(NTK))THEN
          IF(ALAVGK.LE.ALK(1))THEN
```

```fortran
         CK(I)=KP(NTK,1)+(TAVGK-TK(NTK))*(KP(NTK,1)-KP(NTK-1,1))/
     &   (TK(NTK)-TK(NTK-1))+(ALAVGK-ALK(1))*(KP(NTK,2)-KP(NTK,1))/
     &   (ALK(2)-ALK(1))
         ENDIF
         IF(ALAVGK.GT.ALK(1).AND.ALAVGK.LT.ALK(NALK))THEN
           DO N = 1,NALK
           IF(N.NE.NALK)THEN
             IF(ALAVGK.LE.ALK(N+1))THEN
               CK(I)=KP(NTK,N)+(TAVGK-TK(NTK))*(KP(NTK,N)
     &         -KP(NTK-1,N))/(TK(NTK)-TK(NTK-1))+(ALAVGK-ALK(N))
     &           *(KP(NTK,N+1)-KP(NTK,N))/(ALK(N+1)-ALK(N))
             ENDIF
           ENDIF
           ENDDO
         ENDIF
         IF(ALAVGK.GE.ALK(NALK))THEN
           CK(I)=KP(NTK,NALK)+(TAVGK-TK(NTK))*(KP(NTK,NALK)
     &     -KP(NTK-1,NALK))/(TK(NTK)-TK(NTK-1))+(ALAVGK-ALK(NALK))
     &       *(KP(NTK,NALK)-KP(NTK,NALK-1))/(ALK(NALK)-ALK(NALK-1))
         ENDIF
       ENDIF
       ENDIF


C  Next find density-specific heat, CSPD(1) and CSPD(2):

105      DO 50 NC = 1,2

C  For MODEL 1, density-specific heat is a function of temperature only

       IF(MODEL.EQ.1)THEN
         IF(TAVGDC(NC).LE.TDC(1))THEN
           CSPD(I,NC)=DCP(1,1)+(TAVGDC(NC)-TDC(1))*(DCP(2,1)-DCP(1,1))/
     &     (TDC(2)-TDC(1))
         ENDIF

         IF(TAVGDC(NC).GT.TDC(1).AND.TAVGDC(NC).LT.TDC(NTDC))THEN
           DO J = 1,NTDC
           if(j.ne.ntdc)then
             IF(TAVGDC(NC).LE.TDC(J+1))THEN
               CSPD(I,NC)=DCP(J,1)+(TAVGDC(NC)-TDC(J))*(DCP(J+1,1)
     &         -DCP(J,1))/(TDC(J+1)-TDC(J))
             ENDIF
           endif
           ENDDO
         ENDIF


         IF(TAVGDC(NC).GE.TDC(NTDC))THEN
           CSPD(I,NC)=DCP(NTDC,1)+(TAVGDC(NC)-TDC(NTDC))*(DCP(NTDC,1)
     &     -DCP(NTDC-1,1))/(TDC(NTDC)-TDC(NTDC-1))
         ENDIF

       ELSE

C  For MODEL's 2 and 3, find specific heat as a function of temperature
C  and extent of cure

       IF(NTDC.EQ.1.AND.NALDC.EQ.1)THEN
         CSPD(I,NC)=DCP(1,1)
         GO TO 50
       ENDIF
       IF(TAVGDC(NC).LE.TDC(1))THEN
```

```
      IF(ALAVGDC(NC).LE.ALDC(1))THEN
        CSPD(I,NC)=DCP(1,1)+(TAVGDC(NC)-TDC(1))*(DCP(2,1)-DCP(1,1))/
&       (TDC(2)-TDC(1))+(ALAVGDC(NC)-ALDC(1))*(DCP(1,2)-DCP(1,1))/
&       (ALDC(2)-ALDC(1))
      ENDIF
      IF(ALAVGDC(NC).GT.ALDC(1).AND.ALAVGDC(NC).LT.ALDC(NALDC))THEN
        DO N = 1,NALDC
        IF(N.NE.NALDC)THEN
          IF(ALAVGDC(NC).LE.ALDC(N+1))THEN
            CSPD(I,NC)=DCP(1,N)+(TAVGDC(NC)-TDC(1))*(DCP(2,N)-
&           DCP(1,N))/(TDC(2)-TDC(1))+(ALAVGDC(NC)-ALDC(N))*
&           (DCP(1,N+1)-DCP(1,N))/(ALDC(N+1)-ALDC(N))
          ENDIF
          ENDIF
        ENDDO
      ENDIF
      IF(ALAVGDC(NC).GE.ALDC(NALDC))THEN
        CSPD(I,NC)=DCP(1,NALDC)+(TAVGDC(NC)-TDC(1))*(DCP(2,NALDC)-
&       DCP(1,NALDC))/(TDC(2)-TDC(1))+(ALAVGDC(NC)-ALDC(NALDC))*
&       (DCP(1,NALDC)-DCP(1,NALDC-1))/(ALDC(NALDC)-ALDC(NALDC-1))
      ENDIF
    ENDIF

    IF(TAVGDC(NC).GT.TDC(1).AND.TAVGDC(NC).LT.TDC(NTDC))THEN
      DO J = 1,NTDC
      IF(J.NE.NTDC)THEN
        IF(TAVGDC(NC).LE.TDC(J+1))THEN
          IF(ALAVGDC(NC).LE.ALDC(1))THEN
            CSPD(I,NC)=DCP(J,1)+(TAVGDC(NC)-TDC(J))*(DCP(J+1,1)-
&           DCP(J,1))/(TDC(J+1)-TDC(J))+(ALAVGDC(NC)-ALDC(1))*
&           (DCP(J,2)-DCP(J,1))/(ALDC(2)-ALDC(1))
          ENDIF
        IF(ALAVGDC(NC).GT.ALDC(1).AND.ALAVGDC(NC).LT.ALDC(NALDC))THEN
            DO N = 1,NALDC
            IF(N.NE.NALDC)THEN
              IF(ALAVGDC(NC).LE.ALDC(N+1))THEN
                CSPD(I,NC)=DCP(J,N)+(TAVGDC(NC)-TDC(J))*(DCP(J+1,N)-
&               DCP(J,N))/(TDC(J+1)-TDC(J))+(ALAVGDC(NC)-ALDC(N))*
&               (DCP(J,N+1)-DCP(J,N))/(ALDC(N+1)-ALDC(N))
              ENDIF
              ENDIF
            ENDDO
          ENDIF
          IF(ALAVGDC(NC).GE.ALDC(NALDC))THEN
            CSPD(I,NC)=DCP(J,NALDC)+(TAVGDC(NC)-TDC(J))*(DCP(J+1,
&           NALDC)-DCP(J,NALDC))/(TDC(J+1)-TDC(J))+(ALAVGDC(NC)-
&           ALDC(NALDC))*(DCP(J,NALDC)-DCP(J,NALDC-1))/(ALDC(NALDC)-
&           ALDC(NALDC-1))
          ENDIF
        ENDIF
        ENDIF
      ENDDO
    ENDIF

    IF(TAVGDC(NC).GE.TDC(NTDC))THEN
      IF(ALAVGDC(NC).LE.ALDC(1))THEN
        CSPD(I,NC)=DCP(NTDC,1)+(TAVGDC(NC)-TDC(NTDC))*(DCP(NTDC,1)-
&       DCP(NTDC-1,1))/(TDC(NTDC)-TDC(NTDC-1))+(ALAVGDC(NC)-ALDC(1))
&       *(DCP(NTDC,2)-DCP(NTDC,1))/(ALDC(2)-ALDC(1))
      ENDIF
      IF(ALAVGDC(NC).GT.ALDC(1).AND.ALAVGDC(NC).LT.ALDC(NALDC))THEN
        DO N = 1,NALDC
        IF(N.NE.NALDC)THEN
```

```fortran
            IF (ALAVGDC(NC).LE.ALDC(N+1)) THEN
               CSPD(I,NC)=DCP(NTDC,N)+(TAVGDC(NC)-TDC(NTDC))*
     &         (DCP(NTDC,N)-DCP(NTDC-1,N))/(TDC(NTDC)-TDC(NTDC-1))+
     &         (ALAVGDC(NC)-ALDC(N))*(DCP(NTDC,N+1)-DCP(NTDC,N))/
     &         (ALDC(N+1)-ALDC(N))
            ENDIF
            ENDIF
          ENDDO
        ENDIF
        IF (ALAVGDC(NC).GE.ALDC(NALDC)) THEN
          CSPD(I,NC)=DCP(NTDC,NALDC)+(TAVGDC(NC)-TDC(NTDC))*
     &      (DCP(NTDC,NALDC)-DCP(NTDC-1,NALDC))/(TDC(NTDC)-TDC(NTDC-1))+
     &      (ALAVGDC(NC)-ALDC(NALDC))*(DCP(NTDC,NALDC)-DCP(NTDC,NALDC-1)
     &      )/(ALDC(NALDC)-ALDC(NALDC-1))
        ENDIF
      ENDIF
      ENDIF
50    CONTINUE
100   CONTINUE

      do i = 1,mp1
        DO KK = 1,2
          CSPD(I,KK) = CSPD(I,KK)*cc/dt
        ENDDO
      enddo
      RETURN
      END


C ********************************************************************

      subroutine output(nprint,headtq,t,tavg,time,al,alavg,al_5,dal_5,
     1      val)

      parameter(maxp=100,maxm=101)

      integer model

      double precision al(maxM),abcd,alavg,val,tavg,tavg1,abc(5),time,
     1      T(MAXM,2),AL_5(MAXM),DAL_5(MAXM)

      character outfil*12,hh11*29,hh22*21,prunit*6

C Declare variables in common statements

C   Common block /ttl/
      character title*20,ttlfil*4,ttlprp*4,ttlkin*4

C   Common block /kin/

      DOUBLE PRECISION A1,A2,EA1,EA2,M0,M1,DENS,HT,VA1,VA2,VEA1,
     1      VEA2,A3,EA3,D0,D1,D2

C   Common block /prop/
      INTEGER NTDC,NALDC,NTK,NALK
      DOUBLE PRECISION dcp(10,10),tdc(10),aldc(10),kp(10,10),tk(10),
     &alk(10)

C   Common block /bound/
      INTEGER IBC1,IBC2,NBC1,NBC2
      DOUBLE PRECISION TI,TQ1(MAXP),TQ2(MAXP),TIME1(MAXP),TIME2(MAXP)

C   Common block /geom/
      INTEGER ISHAPE,ISYM,M,MP1,ISTEP
```

```
      DOUBLE PRECISION H,L,DZ

C     Common block /tim/
      DOUBLE PRECISION DT,TTIME,PDT

      common/ttl/title,ttlfil,ttlprp,ttlkin,
     &/mod/model,
     &/KIN/A1,A2,EA1,EA2,M0,M1,DENS,HT,VA1,VA2,VEA1,VEA2,A3,EA3,D0,D1,D2
     &/prop/dcp,tdc,aldc,kp,tk,alk,ntdc,naldc,ntk,nalk,
     &/bound/ibc1,ibc2,nbc1,nbc2,ti,TQ1,TQ2,time1,time2,
     &/geom/ISHAPE,ISYM,M,MP1,ISTEP,H,L,DZ,
     &/TIM/TTIME,DT,PDT


C  NPRINT = 0 if printing input parameters and headings
C  NPRINT = 1 if printing temperature and/or extent of cure
C  NPRINT = 2 if printing end line

      IF(NPRINT.EQ.0)THEN
        GO TO 1100
      ELSE
        if(nprint.eq.1)then
          go to 1200
        else
          go to 1300
        endif
      endif
 1100 write(outfil,1000)ttlfil,'out.dat'
 1000 format(' ',a,a)
      open(unit=12,name=outfil(1:12),type='new',carriagecontrol='list')
      write(12,1)title
1     format(' ',3x,'Title: ',a20,/3x,'-----',//,14x,'Input Para',
     +'meters',/,14x,16('-')/)
      if(model.ne.1)then
      write(12,3)'Kinetic Parameters; Extent of Cure < 0.5:'
3     format(' '/,' ',A,/)
      write(12,5)'Pre-exponential factor, Ln(A1),(Ln(1/sec)).',LOG(A1)
      write(12,5)'                        Ln(A2),(Ln(1/sec)).',LOG(A2)
      abcd=ea1/1000.0d0
      write(12,6)'Activation energy const., Ea1, (kJ/mole)...',abcd
6     format(3x,A,f8.2)
      abcd=ea2/1000.0d0
      write(12,6)'                          Ea2, (kJ/mole)...',abcd
      write(12,4)'Exponent, M0, (dimensionless)..............',M0
      write(12,4)'          M1, (dimensionless)..............',M1
4     format(3x,A,e10.4)
      write(12,3)'Extent of Cure > 0.5:'
      write(12,5)'Pre-exponential factor, Ln(A3),(Ln(1/sec)).',LOG(A3)
      abcd=ea3/1000.0d0
      write(12,6)'Activation energy const., Ea3, (kJ/mole)...',abcd
      write(12,4)'Diffusion constant, D0, (dimensionless)....',D0
      write(12,4)'                    D1, (dimensionless)....',D1
      write(12,4)'                    D2, (dimensionless)....',D2
      WRITE(12,7)'Density (kg/m3)............................',DENS
7     FORMAT(/,3X,A,F10.1)
      WRITE(12,7)'Total heat of reaction (J/kg)..............',HT
      if(model.eq.3)then
      abcd=vA1**0.50d0
      write(12,5)'St. dev. of rate constant, A1, (1/sec).....',abcd
5     FORMAT(3X,A,F8.4)
      abcd=vA2**0.50d0
      write(12,5)'St. dev. of rate constant, A2, (1/sec).....',abcd
      abcd=vea1**0.50d0/1000.0d0
      write(12,5)'St. dev. of Ea1 (kJ/mole)..................',abcd
```

```
      abcd=veal**0.50d0/1000.0d0
      write(12,5)'St. dev. of Ea2 (kJ/mole)..................',abcd
      endif
      endif
      write(12,10)'Thermal Properties'
10    format(' ',/,' ',A,/)
      write(12,11)'Thermal conductivity table:'
11    format(3x,A)
      if(model.eq.1)then
      do i = 1,ntk
        write(12,12)tk(i),'C',kp(i,1),'W/mC'
12      format(6x,f6.2,1x,a,2x,f6.2,1x,a)
      enddo
      else
      do i = 1,ntk
        write(12,13)tk(i),'C',(alk(n),kp(i,n),n = 1,nalk)
13      format(5x,f6.2,a,2(3x,F6.3,3X,f6.2,'W/mC'),4(/,12x,
     &  2(3x,F6.3,3X,f6.2,'W/mC')))
      enddo
      endif
      write(12,14)
14    format(' ',/)
      write(12,11)'Density-Specific Heat table:'
      if(model.eq.1)then
      do i = 1,ntdc
        write(12,15)tdc(i),'C',dcp(i,1),'m/s2'
15      format(6x,f6.2,1x,a,2x,E10.4,1x,a)
      enddo
      else
      do i = 1,ntdc
        write(12,16)tdc(i),'C',(ALDC(n),DCP(I,n),n = 1,naldc)
16      format(5x,f6.2,a,2(3x,f6.3,3X,E10.4,'m/s2'),4(/,12x,
     &  2(3x,f6.3,3X,E10.4,'m/s2')))
      enddo
      endif
      write(12,14)
      abcd=ti-273.150d0
      write(12,17)abcd
17    format(' ',/,' ','Initial Condition:',/,' ',2x,'Product temp.'
     +,' (C) at time=0 ...........',f6.2)

c product geometry


      if(Ishape.eq.1)then
      if(Isym.eq.1)l = l*2.0d0
      write(12,18)l
18    format( ' ',/,' ','Slab Geometry:',/,3x,'thickness (m)',
     +26('.'),f10.6)
      else
      if(Ishape.eq.2)then
      write(12,20)l
20    format(' ',/,' ','Cylindrical Geometry:',/,3x,'radius (m)',
     +29('.'),f10.6)
      else
      write(12,22)l
22    format(' ',/,' ','Spherical Geometry:',/,3x,'radius (m)',
     +29('.'),f10.6)
      endif
      endif


c boundary conditions
```

```
      if(Ibc1.eq.1)then
        write(12,23)'Temperature Boundary Condition (IBC1)'
23      format(' ',/,3x,a,/)
      else
        write(12,23)'Heat Flux Boundary Condition (IBC1)'
      endif
      do i = 1,nbc1
        if(Ibc1.eq.1)then
        write(12,24)'Temperature (C) at ',time1(i),' sec.....',tQ1(i)
24      format(6x,a,f8.1,a,f9.2)
        else
        write(12,24)'Heat Flux (W/m2) at ',time1(i),' sec.....',TQ1(i)
        endif
      enddo


      if(Ibc2.eq.1)then
        write(12,23)'Temperature Boundary Condition (IBC2)'
      else
        write(12,23)'Heat Flux Boundary Condition (IBC2)'
      endif
      do i = 1,nbc2
        if(Ibc2.eq.1)then
        write(12,24)'Temperature (C) at ',time2(i),' sec.....',
     &TQ2(i)-273.15D0
        else
        write(12,24)'Heat Flux (W/m2) at ',time2(i),' sec.....',TQ2(i)
        endif
      enddo


c  Temperature history

      write(12,100)title
100 format(' ',//,' ','Title= ',a20,/)
      if(Isym.eq.1)then
      write(12,110)
110 format(' ','Note: Distribution is symmetrical;'/,6x,'results',
     +' are shown for half-thickness only.'/)
      endif

      hh22='DISTRIBUTION HISTORY'
      if(headtq.eq.1)then
        hh11='          TEMPERATURE (C)          '
      else
        hh11='TEMPERATURE (C) & EXTENT OF CURE'
      endif
      write(12,120)hh11,hh22
120 format(' ',/,' ',17x,a,/,23x,a,/,19x,27('-'),/)
      if(model.eq.1)then
        write(12,130)
130 format(' ',32x,'position (m)',/' ',7x,'time',5x,':',40x,
     &'|Avg Temp')
      else
        write(12,135)
135 format(' ',32x,'position (m)',/' ',7x,'time',5x,':',40x,
     &'|Avg Temp ')
      endif
      do i = 1,5
        abc(i)=(i-1)*ISTEP*dz
      enddo
      if(model.eq.1)then
        write(12,137)abc(1),abc(2),abc(3),abc(4),abc(5)
137 format(' ',16x,':',5(f8.4))
      else
```

```fortran
      if(model.eq.2)then
      write(12,140)abc(1),abc(2),abc(3),abc(4),abc(5)
  140 format(' ',16x,':',5(f8.4),'|Ext Cure')
      else
      write(12,145)abc(1),abc(2),abc(3),abc(4),abc(5)
  145 format(' ',16x,':',5(f8.4),'|Ext Cure| StD(%)')
      endif
      endif
      if(model.ne.3)then
      write(12,150)
  150 format(' ',67('='))
      else
        write(12,155)
  155   format(' ',72('='))
      endif

c Printout time heading

 1200 tavg1 = tavg-273.150d0
      do i = 1,5
        abc(i)=t((i-1)*ISTEP+1,2)-273.150d0
      enddo
      prunit = '  sec:'
      write(12,190)time,prunit,abc(1),abc(2),abc(3),abc(4),abc(5),
     &tavg1
  190 format(' ',f10.2,1x,a,5(f7.2,1x),'|',f7.2,'C')

      if(headtq.eq.2)then

C Printout extent of cure values

        do i = 1,5
          abc(i)=al((i-1)*ISTEP+1)
        enddo
        if(model.eq.2)then
          write(12,210)abc(1),abc(2),abc(3),abc(4),abc(5),alavg
  210     format(17x,':',5(f7.3,1x),'|',1x,f7.3)
        else
          write(12,215)abc(1),abc(2),abc(3),abc(4),abc(5),alavg,
     &        (val)**0.50d0
  215     format(17x,':',5(f7.3,1x),'|',f7.3,1x,'|',f6.3)
        endif
      endif
      return


c Printout end line

 1300 if(model.ne.3)then
        write(12,300)
  300   format(' ',67('-'))
      else
        write(12,305)
  305   format(' ',72('-'))
      endif
      close(unit=12)
      return
      end


c
c
c      program RANDNU
```

```
      SUBROUTINE RANDNU(TCC,ntc,iii,sigma,IAR)
C
C......SUBROUTINE FOR GENERATING PSEUDO-RANDOM NUMBERS FROM NORMAL
C......DISTRIBUTION WITH ZERO MEAN AND UNITY VARIANCE.
C
      DOUBLE PRECISION  U(500),XP(500),TCC(12),SIGMA
      DATA A0,A1,B1,B2 /2.30753,0.27061,0.99229,0.04481/
C
      IAR=IAR+iii
C
C......GENERATION OF A SEQUENCE OF PSEUDO-RANDOM NUMBERS OF UNIFORM
C......DISTRIBUTION ON THE INTERVAL (0,1)).
C
      DO 10 I=1,Ntc
10    U(I)=RAN(IAR)
C
C -----------------------------------------------
C
C......GENERATION OF PSEUDO-RANDOM NUMBERS FROM NORMAL DISTRIBUTION,
C......WITH ZERO MEAN AND UNITY VARIANCE,USING INVERSE METHOD(EQ.26.2.23;
C......ABRAMOWITZ AND STEGUN).
C
      DO 20 J=1,Ntc
C
      IF ( U(J) .GT. 0.5 ) THEN
       TEMPU=1.0 - U(J)
       SIGN=-1.
      ELSE
       TEMPU= U(J)
       SIGN=1.
      ENDIF
C
      T=SQRT(ALOG(1.0/TEMPU**2))
      XP(J)=T-(A0+A1*T)/(1.+B1*T+B2*T**2)
      XP(J)=SIGN*XP(J)*sigma
      TCC(j) = TCC(j)+xp(j)
20    continue
C
      RETURN
      END
```

```
c                                         \   __
c@@@@@@@@@@@@@@@@@@@@@@@@@@@@    ___\ /___\  @@@@@@@@@@@@@@@@@@@@@@@@@@@@@@
c..........................  /    \|\___/  ..............................
c!!!!!!!!!!!!!!!!!!!!!!!!!!  /    /     \  !!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!
c//////////////////////// |    | @ -< |  \\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\
c\\\\\\\\\\\\\\\\\\\\\\\\\ |    | \_/  | //////////////////////////////
c!!!!!!!!!!!!!!!!!!!!!!!!!! \     \     / !!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!
c..........................  _____/  ...........................EPS
c@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@
```

APPENDIX B

APPENDIX B

DATA ACQUISITION PROGRAM, *DATA_DA_AD*

B.1 Summary of Program

The data acquisition program, *DATA_DA_AD*, discussed in Chapter 4, is presented in this appendix. An outline of the program is given in Table B.1, and a listing of the program, written in Fortran 77 for a VaxstationII/GPX microcomputer is given in Table B.1.

Table B.1 Description of the Data Acquisition Program, *DATA_DA_AD*.

Subroutine Title	Description
PROGRAM DATA	Main program; contains data acquisition control software.
SUBROUTINE AUTO_ZERO	Calculates zeros (0°C) of amplifiers.
SUBROUTINE PROCESS_DATA	Averages and converts A/D data to temperature and heat flux.
SUBROUTINE SETUP_AMP	Sets gains, weights, and zeros for amplifiers.
SUBROUTINE SETUP_DATA	Initial set-up routine for data acquisition.
SUBROUTINE SETUP_POWER	Data input for D/A power supply.
SUBROUTINE TRANS_ADC	Converts binary data into volts.
SUBROUTINE TRANS_DAC	Converts volts into binary format.

B.2 Program Listing for *DATA_DA_AD.FOR*

```
        PROGRAM DATA
c
c-------------------------------------------------------------------------
c
c  This program was written by Elaine Scott, 7/15/89, with the invaluble
c      help of Mike McPherson of the MSU Case Center.  It is based
c      partly on Example 4-16, pages 4-217-219, VAXlab/LabStar Program-
c      mers Guide.
c
c  The purpose of this program is to read data from the A/D converters
c      on the AXV11-Ca and AXV11-Cb boards, while writing to the D/A on
c      the AXV11-Cb board.
c
c  The program is designed to read thermocouple measurements (mV) and
c      write voltages to a power supply to activate a heater.  The
c      output voltages of the power supply are also read.  The thermo-
c      couple measurements are converted to degrees centigrade (Type E
c      TC), and are written to a file along with the power supply out-
c      put.  The file is compatible to the format required by the
c      parameter estimation program, PROP1D.
c
c  Other features of this program include data averaging over sampling
c      interval and automatic 'zeroing' of input temperature data.
c
c-------------------------------------------------------------------------
c
        IMPLICIT NONE
c
c  Six external functions are used.  Page numbers in descriptions refer
c      to the Vaxlab/LabStar Programmers guide.
c
        EXTERNAL LIO$ATTACH     !Returns the device ID for the specified
                                 device.  See pages 4-48 to 4-51.
        EXTERNAL LIO$DETACH     !Detaches the specified device, returns
c                                any associated storage to the system,
c                                and closes and deallocates associated
c                                VMS devices.  See page 4-54.
        EXTERNAL LIO$READ       !Fills a buffer with data from the spe-
c                                cified device.  See pages 4-58 to 4-59.
        EXTERNAL LIO$SET_I      !Sets up a device according to a parame-
c                                ter code and any number of interger
c                                values.  See pages 4-60 to 4-61.
        EXTERNAL LIO$SET_R      !Sets up a device according to a parame-
c                                ter code and any number of real values.
c                                See pages 4-62 to 4-63.
        EXTERNAL LIO$WRITE      !Empties a buffer through the specified
c                                device.  See pages 4-68 to 4-69.
c
c  Include library containing external functions
c
        INCLUDE 'SYS$LIBRARY:LIOSET.FOR'        !External function symbol
c                                                definitions
c
c  Define external functions
c
        INTEGER*4 LIO$ATTACH, LIO$DETACH, LIO$READ, LIO$SET_I,
        1       LIO$SET_R, LIO$WRITE

c
```

```
c  Declare integer variables
c
      INTEGER          AXA_ID              !AXV11-Ca device ID variable
      INTEGER          AXB_ID              !AXV11-Cb device ID variable
      INTEGER          AD_LENGTH_AXA       !no. of data pts read (AXA)
      INTEGER          AD_LENGTH_AXB       !no. of data pts read (AXB)
      INTEGER*2        BUFF_AD_AXA(8)      !8 word buffer for A/D
      INTEGER*2        BUFF_AD_AXB(8)      !8 word buffer for A/D
      INTEGER*2        BUFF_DA_AXB(500)    !500 word buffer for D/A
      INTEGER          CAL_ZERO            !=1 for calculating zeros
      INTEGER          CLK_ID              !KWV11-C clock ID variable
      INTEGER          I,J,K,DUMMY         !Dummy variables
      INTEGER          NAVG                !Total no. of data averaged
      INTEGER          NCHAN,NCHANA,NCHANB !No. channels (total, board)
      INTEGER          NDATAP              !Total no. data points
      INTEGER          NSAMPL              !No. data avg./samp. interval
      INTEGER          NSTEPS              !No. time steps for zeroing
      INTEGER*4        NVOLT               !No. voltages to be converted
      INTEGER          POWER               !Indicates use of D/A
      INTEGER          STATUS              !Status returned by LIO$
c
c  Declare real variables
c
      REAL*4           GAIN(16)            !Gains for amplifiers
      REAL             HEAT_AREA           !Area of heated surf. (m*m)
      REAL             RATE                !Clock rate (Hertz)
      REAL             RESIST              !Resistance of heater (ohms)
      REAL             SRATE               !Interval rate
      REAL             TIMES(100)          !Times(s) for power supply
      REAL             VOLTS(100)          !Volts(v) for power supply
      REAL*4           WEIGH(16)           !Weights for amplifiers
      REAL*4           ZERO(16)            !Zeros for amplifiers
c
c  Declare character variables
c
      CHARACTER*15     AMP(16)             !Ectron amplifier number
      CHARACTER        BINARYFIL*20        !Binary data file
      CHARACTER        TEMPFIL*20          !Temperature data file
      CHARACTER        YN*2                !Yes/No (Y/N)
c
c  Common statements
c
      COMMON /AMPLIFIER/ GAIN,WEIGH,ZERO,NAVG,NSTEPS,AMP
      COMMON /FILES/BINARYFIL,TEMPFIL
      COMMON /POWER/ BUFF_DA_AXB,NVOLT,POWER,HEAT_AREA,TIMES,VOLTS,
     1      RESIST
      COMMON /SETUP/NCHAN,NCHANA,NCHANB,NDATAP,NSAMPL,RATE,SRATE
c
c*******************************************************************
c
c  Call SETUP_DATA to begin set up for data
c
      CALL SETUP_DATA
c
c  Call SETUP_POWER to begin set up for input to D/A for power supply
c
      WRITE(*,10)'Do you want to input voltage values for D/A?'
     1        ,'   (N = no; F = enter data file; K = use keyboard)'
10    FORMAT(' ',/,' ',5X,A,/,' ',5X,A)
      READ(*,1)YN
1        FORMAT(A)
      IF(YN.NE.'N'.AND.YN.NE.'n')THEN
        CALL SETUP_POWER(YN)
```

```
      ELSE
        POWER = 0
      ENDIF
c
c  Call SETUP_AMP to change gains, weights and/or zeros of amplifiers
c
      CALL SETUP_AMP(NCHAN,CAL_ZERO)
c
c  Name output file for binary and temperature measurements.  Binary
c     data is stored during the experiment in case of unintended
c     program interuption.
c
      WRITE(*,30)'Two data files (binary and temp.) are created:'
30    FORMAT(' ',/,' ',72('*'),/,' ',5X,A)
      WRITE(*,20)'File name for binary data file:'
      READ(*,1)BINARYFIL
      WRITE(*,20)'File name for temperature data file:'
20    FORMAT(' ',/,' ',5X,A)
      READ(*,1)TEMPFIL
c
c  End subroutine set up calls
c
c*********************************************************************
c
c  Begin hardware set up for data aquisition:
c
      WRITE(*,20)'Begin hardware set up:'
c
c  First, attach devices:
c
c  Attach the KWV11-C clock
c     Gets a device ID for the KWV and tells LIO to use QIO I/O
c
      STATUS = LIO$ATTACH(CLK_ID, 'KZA0', LIO$K_QIO)    !Attach to KWV
             IF(.NOT.STATUS)         CALL LIB$SIGNAL(%VAL(STATUS))
c
c-------------------------------------------------------------------
c
c  Attach AXV11-Ca device for A/D
c     Gets a device ID for the AXVa and tells LIO to use QIO I/O
c
      STATUS = LIO$ATTACH(AXA_ID, 'AXA0', LIO$K_QIO)    !Attach to AXVa
             IF(.NOT.STATUS)         CALL LIB$SIGNAL(%VAL(STATUS))
c
c-------------------------------------------------------------------
c
c  Attach AXV11-Cb device for A/D and D/A
c     Gets a device ID for the AXVb and tells LIO to use QIO I/O
c
      IF(NCHANB.GT.0.OR.POWER.EQ.1)THEN
        STATUS = LIO$ATTACH(AXB_ID, 'AXB0', LIO$K_QIO) !Attach to AXVb
             IF(.NOT.STATUS)         CALL LIB$SIGNAL(%VAL(STATUS))
      ENDIF
c
c*********************************************************************
c
c  Set up the clock
c     rate = Hertz rate (a real number)
c     function = repeat count
c     trigger = immediate (this only sets up the start condition, the
c               clock will be started by the LIO$READ from the A/D)
c
      STATUS = LIO$SET_R(CLK_ID, LIO$K_CLK_RATE, 1, RATE)
```

```
                IF(.NOT.STATUS)          CALL LIB$SIGNAL(%VAL(STATUS))
          STATUS = LIO$SET_I(CLK_ID, LIO$K_FUNCTION, 1, LIO$K_REP_COUNT)
                IF(.NOT.STATUS)          CALL LIB$SIGNAL(%VAL(STATUS))
          STATUS = LIO$SET_I(CLK_ID, LIO$K_TRIG, 1, LIO$K_IMMEDIATE)
                IF(.NOT.STATUS)          CALL LIB$SIGNAL(%VAL(STATUS))
c
c*********************************************************************
c
c   Set up AXVa and AXVb:
c
c   AXVa:
c     Sychronous interface (LIO$READ):
c
          STATUS = LIO$SET_I(AXA_ID, LIO$K_SYNCH, 0)
                IF(.NOT.STATUS)          CALL LIB$SIGNAL(%VAL(STATUS))
c
c     Set up A/D:
c     use A/D channels 0-7, depending on value of NCHANA
c
          STATUS = LIO$SET_I(AXA_ID, LIO$K_AD_CHAN, NCHANA, 0, 1, 2, 3,
     1          4, 5, 6, 7)
                IF(.NOT.STATUS)          CALL LIB$SIGNAL(%VAL(STATUS))
c
c     use a gain of one
c
          STATUS = LIO$SET_I(AXA_ID, LIO$K_AD_GAIN, NCHANA, 1, 1, 1, 1,
     1          1, 1, 1, 1)
                IF(.NOT.STATUS)          CALL LIB$SIGNAL(%VAL(STATUS))
c
c     Sweep through all channels on each clock tic:
c
          STATUS = LIO$SET_I(AXA_ID, LIO$K_TRIG, 1, LIO$K_CLK_SWEEP)
                IF(.NOT.STATUS)          CALL LIB$SIGNAL(%VAL(STATUS))
c
c   End AXVa set up
c
c-------------------------------------------------------------------
       IF(NCHANB.GT.0.OR.POWER.EQ.1)THEN
c   AXVb:
c     Sychronous interface (LIO$READ):
c
           STATUS = LIO$SET_I(AXB_ID, LIO$K_SYNCH, 0)
                IF(.NOT.STATUS)          CALL LIB$SIGNAL(%VAL(STATUS))
c
c   Set up A/D:
c     Note, channel 4 is reserved for reading output of power supply,
c     and channels 0-3 are for thermocouple output.  QIO I/O requires
c     channels to be in consecutive, ascending order; therefore, the
c     fifth channel is designated for the power supply, instead of
c     the last, and all five channels must be read regardless whether
c     or not they are all used.
c
c   WARNING:  If additional amplifiers are installed, the channel
c     designation must be changed!!
c
           STATUS = LIO$SET_I(AXB_ID, LIO$K_AD_CHAN, 5, 0, 1, 2, 3, 4)
                IF(.NOT.STATUS)          CALL LIB$SIGNAL(%VAL(STATUS))
c
c     use a gain of one
c
           STATUS = LIO$SET_I(AXB_ID, LIO$K_AD_GAIN, 5, 1, 1, 1, 1, 1)
                IF(.NOT.STATUS)          CALL LIB$SIGNAL(%VAL(STATUS))
c
```

```
c  Set up D/A:
c    use D/A channel X
c
       STATUS = LIO$SET_I(AXB_ID, LIO$K_DA_CHAN, 1, 1)
            IF(.NOT.STATUS)          CALL LIB$SIGNAL(%VAL(STATUS))
c
c  Use immediate start burst mode for AXV11-Cb.  This starts immediately
c    on the LIO$READ call for the AXV11-Ca board:
c
       STATUS = LIO$SET_I(AXB_ID, LIO$K_TRIG, 1, LIO$K_IMM_BURST)
            IF(.NOT.STATUS)          CALL LIB$SIGNAL(%VAL(STATUS))
      ENDIF
c
c  End AXVb set up
c
c*********************************************************************
c
c  Initialize the power supply and open output file before starting the
c    clock:
c
      IF(POWER.EQ.1)THEN
        STATUS = LIO$WRITE(AXB_ID,BUFF_DA_AXB(1),2,LIO$K_OUTPUT)
            IF(.NOT.STATUS)          CALL LIB$SIGNAL(%VAL(STATUS))
      ENDIF
c
      OPEN(UNIT=10,NAME=BINARYFIL,TYPE='NEW',ERR=99)
c
c  Now, initialize the experiment:
c
      WRITE(*,40)'Type "1 <CR>" to start data collection'
40    FORMAT(' ',/,' ',72('*'),/,' ',15X,A,/,' ',72('*'),/)
        READ *,DUMMY
c
c--------------------------------------------------------------------
c
c  Start the clock:
c
      STATUS = LIO$SET_I(CLK_ID, LIO$K_START,0)
            IF(.NOT.STATUS)          CALL LIB$SIGNAL(%VAL(STATUS))
c
c--------------------------------------------------------------------
c
c  Start loop:
c
      K = 2
      DO I = 1,NDATAP
c
c    Write D/A values to power supply using AXVb
c
        IF(POWER.EQ.1)THEN
          IF(K.LE.NVOLT-1)THEN
          IF(TIMES(K).GE.I/RATE.AND.TIMES(K).LT.(I+1)/RATE)THEN
            STATUS = LIO$WRITE(AXB_ID,BUFF_DA_AXB(K),2,LIO$K_OUTPUT)
              IF(.NOT.STATUS)          CALL LIB$SIGNAL(%VAL(STATUS))
            K = K+1
          ENDIF
          ENDIF
        ENDIF
c
c    Read A/D values from thermocouples (channels 0-7 on AXVa and 0-3 on
c    AXVb) and power supply (channel 4 on AXVb)
c
        STATUS = LIO$READ(AXA_ID, BUFF_AD_AXA(1),
```

```
      1         2*NCHANA, AD_LENGTH_AXA, LIO$K_INPUT)
                IF(.NOT.STATUS)          CALL LIB$SIGNAL(%VAL(STATUS))
c
c  Read all data for channel B
c
c  WARNING:  If additional amplifiers are installed, the number of
c     channels read must be changed!!
c
         IF(NCHANB.GT.0.OR.POWER.EQ.1)THEN
           STATUS = LIO$READ(AXB_ID, BUFF_AD_AXB(1),
      1         2*5, AD_LENGTH_AXB, LIO$K_INPUT)
                IF(.NOT.STATUS)          CALL LIB$SIGNAL(%VAL(STATUS))
         ENDIF
c
c     Write data to file: The data from the AXV11-Ca are written on
c        the first line, and the data from the AXV11-Cb, including
c        output from the D/A, are written on the next line.
c
         WRITE(*,50)I,(BUFF_AD_AXA(J), J = 1,NCHANA),
      1        (BUFF_AD_AXB(J), J = 1,NCHANB),BUFF_AD_AXB(5)
         WRITE(10,60)(BUFF_AD_AXA(J), J = 1,NCHANA),
      1        (BUFF_AD_AXB(J), J = 1,NCHANB),BUFF_AD_AXB(5)
50       FORMAT(' ',I6,2X,8(I5,3X),/,9X,8(I5,3X))
60       FORMAT(' ',8(I5,3X),/,' ',8(I5,3X))
      ENDDO
c
c  End loop
c
c-------------------------------------------------------------------------
c
c  Begin shutdown procedure
c
c     Close binary data file
c
      CLOSE(UNIT=10)
c
c     Terminate input voltage to power supply at the end of the run:
c
      IF(POWER.EQ.1)THEN
        STATUS = LIO$WRITE(AXB_ID,BUFF_DA_AXB(NVOLT),2,LIO$K_OUTPUT)
                IF(.NOT.STATUS)          CALL LIB$SIGNAL(%VAL(STATUS))
      ENDIF
c
c     Detach devices:
c
      STATUS = LIO$DETACH(AXA_ID, )
                IF(.NOT.STATUS)          CALL LIB$SIGNAL(%VAL(STATUS))
      IF(NCHANB.GT.0.OR.POWER.EQ.1)THEN
      STATUS = LIO$DETACH(AXB_ID, )
                IF(.NOT.STATUS)          CALL LIB$SIGNAL(%VAL(STATUS))
      ENDIF
c
c     Stop and detach the clock:
c
      STATUS = LIO$SET_I(CLK_ID,LIO$K_STOP,0)
                IF(.NOT.STATUS)          CALL LIB$SIGNAL(%VAL(STATUS))
      STATUS = LIO$DETACH(CLK_ID, )
                IF(.NOT.STATUS)          CALL LIB$SIGNAL(%VAL(STATUS))
c
c  Data collection is complete
c
      WRITE(*,30)'Data collection is completed, now process data:'
c
```

```
c********************************************************************
c
c  Start data analysis:
c
c     First calculate zeros for amplifiers if needed.
c
       IF(CAL_ZERO.EQ.1)THEN
         CALL AUTO_ZERO(POWER)
       ENDIF
c
c     Now, average binary data over sampling interval, and convert
c       binary data into millivolts and then to degrees centigrade.
c
       CALL PROCESS_DATA(POWER,HEAT_AREA,RESIST)
c
c  All done now.... stop and end
c
       WRITE(*,70)'Program is completed.'
70     FORMAT(//,' ',72('*'),/,' ',5X,A,/)
       GO TO 300
99     STOP       'Error during opening master data file'
300    STOP
       END
c
c     Fini!!
c
c
c********************************************************************
c
c  End main program.
c
c  Begin subroutines:
c     There are six subroutines in this program; they are listed in
c     alphabetical order:
c     Title          Arguments             Brief Description
c_____
c
c  AUTO_ZERO       POWER                 Calculates zeros(0C) of amplifiers
c  PROCESS_DATA    POWER,HEAT_AREA       Avgerages & converts A/D data
c  SETUP_AMP       NCHAN,CAL_ZERO        Sets gain, weight, zero for ampl.
c  SETUP_DATA      (none)                Initial set up for data aquisition
c  SETUP_POWER     YN                    Data input for D/A
c  TRANS_DAC       VOLTS,BUFF_DA_AXB     Converts volts to binary format
c
c********************************************************************
c********************************************************************
c
       SUBROUTINE AUTO_ZERO(POWER)
c
c  This subroutine calculates the zeros (C) for the amplifiers, based
c     on initial isothermal data.
c
       IMPLICIT NONE
c
c  Declare integer values
c
       INTEGER I,J,K            !Dummy
       INTEGER NAVG             !Total no. of data averaged
       INTEGER       NCHAN,NCHANA,NCHANB    !Total number of channels
       INTEGER NDATAP           !Total no. data points
       INTEGER NSAMPL           !No. data avg./samp. interval
       INTEGER NSTEPS           !No. time steps for zeroing
       INTEGER NZERO            !No. of zeros changed
```

```
      INTEGER NWEIGH          !No. of weights changed
      INTEGER POWER           !Indicates use of D/A
c
c  Declare real values
c
      REAL*4             AVGZERO(100,16) !Binary data to be averaged
      REAL*4             CONV(16)        !Inter. value for zeros
      REAL*4             GAIN(16)        !Gains for amplifiers
      REAL               RATE     !Clock rate (Hertz)
      REAL               SRATE           !Interval rate
      REAL               SUMI(16)        !Sum of binary data
      REAL               SUMAVG          !Average binary data
      REAL               SUMWGH          !Average weights
      REAL*4             WEIGH(16)       !Weights for amplifiers
      REAL*4             ZERO(16)        !Zeros for amplifiers
c
c  Declare character values
c
      CHARACTER*15       AMP(16)         !Ectron amplifier number
      CHARACTER          BINARYFIL*20    !Binary data file
      CHARACTER          TEMPFIL*20      !Temperature data file
      CHARACTER          YN*2     !Yes/No (Y/N)
c
c  Common statement
c
      COMMON /AMPLIFIER/ GAIN,WEIGH,ZERO,NAVG,NSTEPS,AMP
      COMMON /FILES/BINARYFIL,TEMPFIL
      COMMON /SETUP/NCHAN,NCHANA,NCHANB,NDATAP,NSAMPL,RATE,SRATE
c
c************************************************************************
c
c  The zero's are calculated internally by averaging the first NSTEPS
c  data points for each thermocouple prior to the onset of applied heat
c  flux, and determining the difference between the overall average and the
c  average value for each thermocouple.
c-----------------------------------------------------------------------
c
c  Read in first NAVG values from binary data file (BINARYFIL)
c
      OPEN(UNIT=20,NAME=BINARYFIL,STATUS='OLD')
      DO J = 1,NSTEPS
         K = (J-1)*NCHAN
        READ(20,*)(AVGZERO(J,I), I = 1,NCHANA)
        IF(NCHANB.GT.0.OR.POWER.EQ.1)THEN
          READ(20,*)(AVGZERO(J,NCHANA+I), I = 1,NCHANB+POWER)
        ENDIF
      ENDDO
c
c  Close binary data file
c
      CLOSE (UNIT=20)
c
c-----------------------------------------------------------------------
c
c
c  Check weights and recalculate zeros if you find bad thermocouples.
c
        WRITE(*,10)'Number','Amplifier','Weighting Factor'
        DO I = 1,NCHAN
          WRITE(*,20)I,AMP(I),WEIGH(I)
        ENDDO
        TYPE *
        WRITE(*,30)'Are corrected weighting factors OK? (Y/N)'
```

```
          READ(*,1)YN
c
c  Change weights if necessary
c
          IF(YN.EQ.'N'.OR.YN.EQ.'n')THEN
100         WRITE(*,30)'Enter number of weights you wish to change:'
            READ *,NWEIGH
            DO I = 1,NWEIGH
              WRITE(*,30)'Enter amplifier number and corrected weight:'
              READ *,J,WEIGH(J)
            ENDDO
            WRITE(*,10)'Number','Amplifier','Corrected Weights'
            DO J = 1,NCHAN
              WRITE(*,20)J,AMP(J),WEIGH(J)
            ENDDO
            WRITE(*,30)'Are corrected weights OK? (Y/N)'
            READ(*,1)YN
            IF(YN.EQ.'N'.OR.YN.EQ.'n')GO TO 100
              ENDIF
        SUMAVG = 0.0D0
        SUMWGH = 0.0D0
        DO I = 1,NCHAN
          SUMI(I) = 0.0D0
            SUMWGH = SUMWGH + WEIGH(I)
        ENDDO
c
c  Average data over all channels for NSTEPS time steps
c
        DO J = 1,NSTEPS
            DO I = 1,NCHAN
            SUMI(I) = SUMI(I) + AVGZERO(J,I)*WEIGH(I)
          ENDDO
        ENDDO
c
c  Adjust for gain
c
        DO I = 1,NCHAN
            SUMAVG = SUMAVG + SUMI(I)*GAIN(I)
          ENDDO
          SUMAVG = SUMAVG/SUMWGH
c
c  Calculate zeros
c
        DO I = 1,NCHAN
            CONV(I) = (SUMAVG-SUMI(I)*GAIN(I))/NSTEPS
        ENDDO
        CALL TRANS_ADC(0,NCHAN,CONV,ZERO)
1       FORMAT(A)
10      FORMAT(' ',/,' ',3X,A,3X,A,7X,A)
20      FORMAT(' ',3X,I6,3X,A,3X,F6.3)
30      FORMAT(' ',/,' ',A)
c
c  End AUTO_ZERO subroutine.
c
        RETURN
        END
c
c*********************************************************************
c*********************************************************************
c
        SUBROUTINE PROCESS_DATA(POWER,HEAT_AREA,RESIST)
c
c  This subroutine averages A/D data over each sampling interval, and
```

```
c     then converts the binary data to millivolts and then to degrees
c     centigrade.
c
      IMPLICIT NONE
c
c  Declare integers variables
c
      INTEGER I,J,K,L          !Dummy variables
      INTEGER NAVG             !Total no. of data averaged
      INTEGER    NCHAN,NCHANA,NCHANB    !No. channels (total, board)
      INTEGER NCHANP1          !Includes voltage channel
      INTEGER NDATAP,NDATA      !Total no. data points
      INTEGER NSAMPL           !No. data avg./(samp intrvl)
      INTEGER NSTEPS           !No. time steps for zeroing
      INTEGER POWER            !=1 for output to D/A
      INTEGER STATUS           !Status returned by LIO$
c
c  Declare real variables
c
      REAL              AVG_DATA(1000)  !Data to be avgeraged
      REAL*4            GAIN(16)       !Gains for amplifiers
      REAL              HEAT_AREA      !Area of heated surf. (m*m)
      REAL              HEAT_FLUX      !Heat flux from heater
      REAL              RATE,SRATE     !Clock rate (Hertz)
      REAL              RESIST         !Resistance of heater (ohms)
      REAL              SUM(16)        !Sums for averaging data
      REAL              TEMP(16)       !Converted temps. from A/D
      REAL              TIMSTP         !Time step for printout
      REAL              VA(16)         !Millivolts from A/D
      REAL*4            WEIGH(16)      !Weights for amplifiers
      REAL*4            ZERO(16)       !Zeros for amplifiers
c
c  Declare character variable
c
      CHARACTER*15      AMP(16)        !Ectron amplifier number
      CHARACTER         BINARYFIL*20   !Binary data file
      CHARACTER         TEMPFIL*20     !Temperature data file
c
c  Common statement
c
      COMMON /AMPLIFIER/ GAIN,WEIGH,ZERO,NAVG,NSTEPS,AMP
      COMMON /FILES/BINARYFIL,TEMPFIL
      COMMON /SETUP/NCHAN,NCHANA,NCHANB,NDATAP,NSAMPL,RATE,SRATE
c
c*********************************************************************
c
c  Open binary data file (BINARYFIL) and temperature data file (TEMPFIL)
c
      OPEN(UNIT=20,NAME=BINARYFIL,STATUS='OLD')
      OPEN(UNIT=30,NAME=TEMPFIL,TYPE='NEW')
c
c  Initialize arrays, etc.
c
      NDATA = NDATAP/NSAMPL
      NCHANP1 = NCHAN + POWER
      DO J = 1,NCHANP1
        SUM(J) = 0
      ENDDO
c
c------------------------------------------------------------------------
c
c  Read in data values from file
c
```

```fortran
      DO L = 1,NDATA
        DO J = 1,NSAMPL
          K = (J-1)*NCHANP1
          READ(20,*,ERR=99)(AVG_DATA(K+I), I = 1,NCHANA),
     1        (AVG_DATA(K+NCHANA+I), I = 1,NCHANB+POWER)
c
c  Average data over sampling interval
c
          DO I = 1,NCHANP1
            SUM(I) = SUM(I) + AVG_DATA(K+I)/NSAMPL
          ENDDO
        ENDDO
c
c ----------------------------------------------------------------------
c
c  Begin processing data
c
c  Convert binary data into volts. Binary data is converted to
c     voltages in subroutine TRANS_ADC assuming a linear relationship
c     between the binary output and volts based on a calibrated curve.
c     Voltage values are returned in VA.
c
        CALL TRANS_ADC(POWER,NCHANP1,SUM,VA)
c
        DO I = 1,NCHANP1
c
c  Next, convert thermocouple values to degrees centigrade if channel is
c     not reading from power supply.
c
          IF(POWER.EQ.1.AND.I.EQ.NCHANP1)GOTO 100
c
c  First, adjust thermocouple data for gain and zeros (C), and then con-
c     vert data to millivolts.
c
          VA(I) = (VA(I)*GAIN(I)+ZERO(I))/1000.0
c
c  Voltages are then converted to temperatures using the thermocouple
c     conversion routine in VAXlab/Lab-Star Programmers Guide.  See
c     Sec. 6.9, pages 6-17 to 6-19; pages 6-62 to 6-63; and Example 6-20
c     on page 6-119 for details.
c
c  Note, this subroutine is for Type E, Chromel-Constantan thermocouples.
c     Input values are the voltages in microvolts, the number of data
c     values to be converted, and output values are temperature in
c     degrees centigrade and the operation status.
c
          CALL LSP$THERMOCOUPLE_E (VA(I),TEMP(I),1,STATUS)
            IF(.NOT.(status))     CALL lib$signal(%val(status))
100     ENDDO
c
c  Print out processed temperature data (C) to file (TEMPFIL)
c
        TIMSTP=SRATE*L
        IF(POWER.NE.1)THEN
          IF(NCHAN.LE.8)THEN
            WRITE(30,10) TIMSTP,(TEMP(I),I=1,NCHAN)
10          FORMAT(F10.3,1X,8(F6.2,1X))
          ELSE
            WRITE(30,20) TIMSTP,(TEMP(I),I=1,NCHAN)
20          FORMAT(F10.3,1X,16(F6.2,1X))
          ENDIF
        ELSE
c
```

```
c  Calculate heat flux using measured voltage and resistance of heater
c     (power = (volts)*(volts)/resistance; heat flux = power/area)
c
          HEAT_FLUX = VA(NCHANP1)*VA(NCHANP1)/(RESIST*HEAT_AREA)
c
c  Write processed heat flux and temperature data to a file
c
          IF(NCHAN.LE.8)THEN
            WRITE(30,30) TIMSTP,HEAT_FLUX,(TEMP(I),I=1,NCHAN)
30          FORMAT(F10.3,1X,F8.1,1X,8(F6.2,1X))
          ELSE
            WRITE(30,40) TIMSTP,HEAT_FLUX,(TEMP(I),I=1,NCHAN)
40          FORMAT(F10.3,1X,F8.1,1X,13(F6.2,1X))
          ENDIF
        ENDIF
c
c  End data processing
c
c ------------------------------------------------------------------
c
c  Initialize summations
c
        DO I = 1,NCHANP1
          SUM(I) = 0.0
          VA(I) = 0.0
        ENDDO
c
c  End loop
c
      ENDDO
c
c*********************************************************************
c
c  Close binary data file and temperature file
c
      CLOSE (UNIT=20)
      CLOSE (UNIT=30)
c
c  End data processing subroutine
c
      RETURN
99    STOP      'Error while reading from data file'
      END
c
c*********************************************************************
c*********************************************************************
c
      SUBROUTINE SETUP_AMP(NCHAN,CAL_ZERO)
c
c  This subroutine sets up the Ectron amplifiers; user may change gains,
c     weights and/or zeros if necessary.
c
      IMPLICIT NONE
c
c
c  Define integer variables
c
      INTEGER CAL_ZERO    !=1 for calculating zeros
      INTEGER         I,J           !Dummy
      INTEGER NAVG        !Total no. of data averaged
      INTEGER NCHAN       !Total number of channels
      INTEGER NGAIN       !No. of gains changed
      INTEGER NSTEPS      !No. of time steps for zeroing
```

```fortran
      INTEGER NWEIGH          !No. of weights changed
      INTEGER NZERO           !No. of zeros changed
c
c  Define real variables
c
      REAL*4             GAIN(16)         !Gains for amplifiers
      REAL*4             WEIGH(16)        !Weights for amplifiers
      REAL*4             ZERO(16)         !Zeros for amplifiers
c
c  Define character variables
c
      CHARACTER*15       AMP(16)          !Ectron amplifier number
      CHARACTER*1        YN               !Yes/no (Y/N)
c
c  Common statement
c
      COMMON /AMPLIFIER/ GAIN,WEIGH,ZERO,NAVG,NSTEPS,AMP
c
c  Data statements for amplifiers
c    Ectron amplifier numbers:
c
      DATA AMP(1),AMP(2),AMP(3),AMP(4),AMP(5),AMP(6),AMP(7),AMP(8),
     1      AMP(9),AMP(10),AMP(11),AMP(12)/'ECTRON_53661',
     1      'ECTRON_53662','ECTRON_53663','ECTRON_53664',
     1      'ECTRON_53665','ECTRON_53674','ECTRON_53675',
     1      'ECTRON_53676','ECTRON_53677','ECTRON_53678',
     1      'ECTRON_53973','ECTRON_53974'/
c
c    Gain of Ectron amplifiers last checked on 3/16/89
c
      DATA GAIN(1),GAIN(2),GAIN(3),GAIN(4),GAIN(5),GAIN(6),GAIN(7),
     1      GAIN(8),GAIN(9),GAIN(10),GAIN(11),GAIN(12)/1.003,1.003,
     1      0.996,0.999,0.998,0.995,1.002,1.000,0.999,0.999,1.028,
     1      1.008/
c
c    Weights of Ectron amplifiers
c
      DATA WEIGH(1),WEIGH(2),WEIGH(3),WEIGH(4),WEIGH(5),WEIGH(6),
     1      WEIGH(7),WEIGH(8),WEIGH(9),WEIGH(10),WEIGH(11),WEIGH(12)
     1      /1.00,1.00,1.00,1.00,1.00,1.00,1.00,1.00,1.00,1.00,1.00,
     1      1.00/
c
c    Zeros are millivolt readings at 0C; last checked on 3/30/89.
c
      DATA ZERO(1),ZERO(2),ZERO(3),ZERO(4),ZERO(5),ZERO(6),ZERO(7),
     1      ZERO(8),ZERO(9),ZERO(10),ZERO(11),ZERO(12)/0.002,0.000,
     1      0.000,-0.003,0.0005,0.001,-0.0025,-0.0005,0.0005,0.005,
     1      0.0055,-0.004/
c
c*******************************************************************
c
c  Set up amplifiers: change gains, weights and/or zeros if necessary:
c
      WRITE(*,10)'Begin set up for amplifiers:'
c
c------------------------------------------------------------------
c
c    Change gain of amplifiers if necessary.  Gains represent fractional
c    output at 10V input (amps should read 0-10V; for example, if the
c    amplifier instead read 0-9.99V, the gain would be 0.999)
c
           WRITE(*,40)'Check gain of Ectron amplifiers:'
        TYPE *
```

```
             WRITE(*,20)'Number','Amplifier','Gain'
             DO J = 1,NCHAN
          WRITE(*,30)J,AMP(J),GAIN(J)
             ENDDO
c
c     You may change any number of gains that you want
c
             WRITE(*,40)'Do you want to change any of the gains? (Y/N)'
        READ(*,1)YN
        IF(YN.EQ.'Y'.OR.YN.EQ.'y')THEN
300     WRITE(*,40)'Enter number of gains you wish to change:'
        READ *,NGAIN
c
c     Amplifier numbers start from 1 and go to 12 (Ectron Amplifiers)
c
        DO I = 1,NGAIN
          WRITE(*,40)'Enter amplifier number and corrected gain:'
          READ*,J,GAIN(J)
        ENDDO
        TYPE *
        WRITE(*,20)'Number','Amplifier','Corrected Gain'
        DO J = 1,NCHAN
          WRITE(*,30)J,AMP(J),GAIN(J)
        ENDDO
c
c     Re-correct values if necessary
c
        WRITE(*,40)'Are corrected gains OK? (Y/N)'
        READ(*,1)YN
        IF(YN.EQ.'N'.OR.YN.EQ.'n')GO TO 300
            ENDIF
c
c----------------------------------------------------------------------
c
c     Change weights for amplifiers if necessary.  Use a weight of 1.0 for
c     good thermocouples, and a weight of 0.0 for bad thermocouples.
c
        WRITE(*,40)'Check weights for Ectron amplifiers:'
        TYPE *
             WRITE(*,50)'Number','Amplifier','Weight'
             DO J = 1,NCHAN
          WRITE(*,60)J,AMP(J),WEIGH(J)
        ENDDO
             WRITE(*,40)'Do you want to change any of the weights? (Y/N)'
             READ(*,1)YN
             IF(YN.EQ.'Y'.OR.YN.EQ.'y')THEN
c
c     Change as many of the weights as you want.
c
400     WRITE(*,40)'Enter number of weights you wish to change:'
        READ*,NWEIGH
c
c     Amplifier numbers range from 1 to 12 (Ectron Amplifiers)
c
        DO I = 1,NWEIGH
          WRITE(*,40)'Enter amplifier number and corrected weight:'
          READ*,J,WEIGH(J)
        ENDDO
        TYPE *
        WRITE(*,20)'Number','Amplifier','Corrected Weight'
        DO J = 1,NCHAN
          WRITE(*,30)J,AMP(J),WEIGH(J)
        ENDDO
```

```
c
c     Re-correct values if necessary
c
         WRITE(*,40)'Are corrected weights OK? (Y/N)'
         READ(*,1)YN
         IF(YN.EQ.'N'.OR.YN.EQ.'n')GO TO 400
      ENDIF
c
c-----------------------------------------------------------------------
c
c  Change zeros of amplifiers if necessary.  Zeros represent the ampli-
c     fier readings at 0C.  There are three options for the user here:
c     1.  use the zeros given; 2. let the program calculate the zeros;
c     3.  enter in zeros.
c
      WRITE(*,40)'Check zeros (at 0C) of Ectron amplifiers:'
      TYPE *
      WRITE(*,20)'Number','Amplifier','mV at 0C'
            DO J = 1,NCHAN
         WRITE(*,70)J,AMP(J),ZERO(J)
            ENDDO
      TYPE *
      WRITE(*,80)'Do you want the zeros to be recalculated for you?',
     1       ' (Y/N)'
            READ(*,1)YN
      CAL_ZERO = 0
      NSTEPS = 0
      NAVG = 0
c
c     If user wants program to calculate zeros, the voltage values are
c     averaged over a number of time steps specified by the user.
c     The time step means the actual time step in which data is col-
c     lected, not the averaged sampling interval.  The temperatures
c     should be isothermal over this interval, with no externally
c     applied heat flux.
c
            IF(YN.EQ.'Y'.OR.YN.EQ.'y')THEN
        WRITE(*,90)'Enter number of time steps to average zeros over:'
     1       ,'(No heat flux should be applied over this interval.)'
        READ *,NSTEPS
        CAL_ZERO = 1
        NAVG = NSTEPS*NCHAN
      ELSE
c
c     User may change zeros by himself or herself
c
         WRITE(*,40)'Do you want to change any of the zeros? (Y/N)'
         READ(*,1)YN
         IF(YN.EQ.'Y'.OR.YN.EQ.'y')THEN
500        WRITE(*,40)'Enter number of zeros you wish to change:'
           READ*,NZERO
           DO I = 1,NZERO
             WRITE(*,40)'Enter amplifier number and corrected zeros:'
             READ *,J,ZERO(J)
           ENDDO
           TYPE *
         WRITE(*,20)'Number','Amplifier','Corrected mV at 0C'
           DO J = 1,NCHAN
             WRITE(*,30)J,AMP(J),ZERO(J)
           ENDDO
c
c     Re-correct values if necessary
```

```
c
          WRITE(*,40)'Are corrected zeros OK? (Y/N)'
            READ(*,1)YN
            IF(YN.EQ.'N'.OR.YN.EQ.'n')GO TO 500
          ENDIF
              ENDIF
1     FORMAT(A)
10    FORMAT(' ',//,' ',72('*'),//,10X,A,//)
20    FORMAT(' ',3X,A,3X,A,7X,A)
30    FORMAT(' ',3X,I6,3X,A,3X,F6.3)
40    FORMAT(' ',/,' ',5X,A)
50    FORMAT(' ',3X,A,3X,A,5X,A)
60    FORMAT(' ',3X,I6,3X,A,3X,F6.4)
70    FORMAT(' ',3X,I6,3X,A,5X,F7.4)
80    FORMAT(' ',/,' ',5X,A,A)
90    FORMAT(' ',/,' ',5X,A,/,' ',5X,A)
c
c     End set up for amplifiers
c
      RETURN
      END
c
c**********************************************************************
c**********************************************************************
c
      SUBROUTINE SETUP_DATA
c
c   This subroutine provides the initial set up for data aquisition:
c
      IMPLICIT NONE
c
c   Define integer variables
c
      INTEGER    NCHAN,NCHANA,NCHANB      !No. channels (total, board)
      INTEGER NDATA             !No. of data pts per channel
      INTEGER NDATAP            !Total no. data points
      INTEGER NSAMPL            !No. data avg/(samp intrvl)
c
c   Define real variables
c
      REAL              RATE     !Clock rate (Hertz)
      REAL              SRATE            !Interval rate
c
c   Define character variable
c
      CHARACTER         YN*2     !Yes/no (Y/N)
c
c   Common statement
c
      COMMON /SETUP/NCHAN,NCHANA,NCHANB,NDATAP,NSAMPL,RATE,SRATE
c
c*********************************************************************
c
c   First set up sampling interval, and number of samples to be averaged
c        over each sampling interval.
c
      WRITE(*,10)'Begin set up for data aquisition'
      WRITE(*,20)'Data is collected over a sampling interval and',
      1      ' averaged for that interval.'
5     WRITE(*,30)'Enter sampling interval in seconds: '
        READ *,SRATE
      WRITE(*,40)'Enter no. of samples to be averaged per sampling ',
      1      'interval:'
```

```fortran
      READ *,NSAMPL
      RATE = 1.0*NSAMPL/SRATE
      WRITE(*,50)'rate =',RATE,' Hertz'
c
c     Next enter total number of data points for each channel and
c     the total number of channels.
c
      WRITE(*,40)'Enter total number of sampling intervals',
     1      ' for each channel:'
      READ*,NDATA
      NDATAP = NDATA*NSAMPL
      WRITE(*,30)'Enter total number of channels (max=12):'
      READ*,NCHAN
      IF(NCHAN.LT.8)THEN
        NCHANA = NCHAN
        NCHANB = 0
      ELSE
        NCHANA = 8
        NCHANB = (NCHAN-8)
      ENDIF
c
c     Allow user to change input values.
c
      TYPE *
      WRITE(*,30)'Do you want to change the above input values? (Y/N)'
      READ(*,1)YN
      IF(YN.EQ.'Y'.OR.YN.EQ.'y')GOTO 5
c
c  Initial set up complete
c
1         FORMAT(A)
10        FORMAT(' ',////,' ',72('*'),//,' ',20X,A,//,' ',72('*'),//)
20        FORMAT(' ',10X,A,/,' ',5X,A,/)
30        FORMAT(' ',5X,A)
40        FORMAT(' ',5X,A,A)
50        FORMAT(' ',/,' ',10X,A,F8.3,A,/)
      RETURN
      END
c
c**********************************************************************
c**********************************************************************
c
      SUBROUTINE SETUP_POWER(YN)
c
c  This subroutine provides the initial set up for input to D/A for
c     power supply.
c
      IMPLICIT NONE
c
c  Define integer variables
c
      INTEGER*2     BUFF_DA_AXB(500)     !500 word buffer for D/A
      INTEGER J                    !Dummy variable
      INTEGER*4     NVOLT               !No. voltages converted
      INTEGER POWER          !Indicates use of D/A
c
c  Define real variables
c
      REAL          HEAT_AREA      !Area of heated surf. (m*m)
      REAL          RESIST         !Resistance of heater (ohms)
      REAL          TIMES(100)     !times(s) for power supply
      REAL          VOLTS(100)     !volts(v) for power supply
c
```

```
c  Define character variables
c
       CHARACTER          POWERFIL*20      !Data file for D/A input
       CHARACTER          YN*2     !Yes/no (Y/N)
c
c  Common statement
c
       COMMON /POWER/ BUFF_DA_AXB,NVOLT,POWER,HEAT_AREA,TIMES,VOLTS,
       1          RESIST
c
c********************************************************************
c
c  Set up program for heat flux:
c
       WRITE(*,10)'Begin set up for D/A to power supply:'
       POWER = 1
c
c  Description of input file.
c
         WRITE(*,20)'A data file is created which contains the ',
       1       'desired input ','voltages for the power supply.  ',
       1       'Set up the file as follows:',
       1       'line 1: Surface area of the heating unit (m*m)',
       1       '         (Divided by two for symmetrical case.)',
       1       'line 2: Total number of voltage data values (NVOLT)',
       1       'line 3: Time (sec), volts','.','.',
       1       'line NVOLT+2: Time (sec), volts ',
       1       'For, example, if you want to read 10 volts to the power',
       1       'supply at 20 sec and then read 0 volts at 40 sec from',
       1       ' the ','start of the experiment, enter in from line ',
       1       '2 to line NVOLT+2:',
       1       'line 2: 2',
       1       'line 3: 20.,10.',
       1       'line 4: 40.,0.'
c
c     Enter file name for input voltage data for power supply
c
       IF(YN.EQ.'F'.OR.YN.EQ.'f')THEN
         WRITE(*,30)'Enter input file name for power supply input:'
           READ(*,1)POWERFIL
         OPEN(UNIT=10,NAME=POWERFIL,STATUS='OLD')
c
c     The heat flux area is area of heated surface (divided by two for
c     the symmetrical case) (m*m).
c
         READ(10,*)HEAT_AREA
c
c     Read the resistance of the heater in ohms.
c
         READ(10,*)RESIST
c
c     Read the total number of voltage D/A input values.
c
         READ(10,*)NVOLT
c
c     Start DO loop for voltages.  The times (sec) and voltages (volts)
c     are read in for the total number of voltage values.
c
c     The actual desired output voltages from the power supply are to
c     be read in.  These values are converted to the output range of
c     the computer (0 to 10 volts), and then a 2:1 divider is used to
c     scale the voltage to the input required voltage for the
c     HP 6024A DC power supply (0 to 5 volts).  The power supply then
```

```
c      scales this input to 0 to 60 volts output to the heater.
c
c      The voltage will commence at the designated time and the signal
c      will continue until changed.  The dummy variable starts from '2'
c      because an initial zero voltage is added later.  A final zero
c      voltage is also added to turn off the power supply at the end
c      of the run.
c
         DO J = 2,NVOLT+1
           READ(10,*)TIMES(J),VOLTS(J)
         ENDDO
       ELSE
c
c   Or, enter voltage data by keyboard.
c      The variables are entered in the same order as described above.
c
c      First, enter heat flux area (m*m).
c
         WRITE(*,30)'Enter area of heated surface (divide by 2) (m*m):'
         READ(*,*)HEAT_AREA
c
c      Next, enter the resistance of the heater (ohms).
c
         WRITE(*,30)'Enter resistance of heater (ohms):'
         READ(*,*)RESIST
c
c      Enter the total number of voltage D/A input values.
c
         WRITE(*,30)'Enter total number of voltage data values:'
         READ(*,*)NVOLT
c
c      Now start the DO loop for D/A voltage data.  See notes above.
c
         WRITE(*,30)'Enter time (sec) and voltage (volts):'
         DO J = 2,NVOLT+1
           WRITE(*,40)J-1
           READ(*,*)TIMES(J),VOLTS(J)
         ENDDO
       ENDIF
c
c   Initialize and shutdown power supply by imposing 0.0 volts at
c      time equal to 0 sec and at end of run.
c
       NVOLT = NVOLT+2
       VOLTS(1) = 0.0
       VOLTS(NVOLT) = 0.0
c
c   Convert voltage input to integer values for D/A;
c      CALL TRANS_DAC subroutine to convert volts in to binary form.
c
       CALL TRANS_DAC(NVOLT,VOLTS,BUFF_DA_AXB)
c
c   End set up for power supply
c
1      FORMAT(A)
10     FORMAT(' ',/,' ',72('*'),/,10X,A,/)
20     FORMAT(11X,A,A,/,6X,A,A,/,7(/,16X,A),//,11X,A,/,6X,A,A,
      1        /6X,A,A,/,3(/,16X,A))
30     FORMAT(' ',/,' ',5X,A)
40     FORMAT(' ',I3,':')
50     FORMAT(' ',F10.2,5X,F10.2,5X,I10)
c
       RETURN
```

```
      END
c
c*********************************************************************
c*********************************************************************
c
      SUBROUTINE   TRANS_DAC(NVOLT,VOLTS,BUFF_DA_AXB)
c
c  This subroutine first scales the input voltage to the output voltage
c     of the VaxII/GPX (0 to 10V), and then converts the voltage
c     values to the binary form required for the D/A converter, using
c     a calibration chart by M. Loh, 7/30/89.  The chart may be
c     found in the data aquisition notebook in RM A-32, RCE, MSU.
c
      IMPLICIT NONE
c
c  Define integer variables
c
      INTEGER*2    BUFF_DA_AXB(500)    !buffer for D/A
      INTEGER J                        !Dummy variable
      INTEGER NVOLT            !Number of D/A voltage data
c
c  Define real variables
c
      REAL              VOLTS(100)        !volts(v) for D/A
      REAL              A                 !Y-intrcpt for volt/bin conv
      REAL              B                 !Slope for volt/binary convr
c
c*********************************************************************
c
c  Based on calibration by M. Loh, scaling factor between the
c     output voltage signal from the VaxII/GPX and the output signal
c     from the HP 6024A DC power supply was found to be 6.012559.  The
c     voltage was found to vary linearly with binary output, over the
c     voltage range from 0 to 10 volts.  The conversion equation is:
c     binary = A + B*volts, where A = 2048.2235, and B = -34.02974.
c
c  Note: 10V is the maximum output for the VaxII/GPX computer. If more
c     than 60 V are read in as output to the power supply, it will be
c     scaled to 10 V for the D/A, and a warning statement will be
c     shown on the screen.
c
      A = 2048.2235
      B = -34.02974
      DO J = 1,NVOLT
c
c  Check to see if input voltage is greater than 60.0V and set to 60.0V
c     if it is. (60V is maximum voltage for HP 6024A power supply.)
c
        IF(VOLTS(J).GT.60.0)THEN
          VOLTS(J)=60.0
          WRITE(*,*)'WARNING: INPUT VOLTAGE GREATER THAN 60V; SET TO',
     1        ' 60V!'
        ENDIF
c
c  Convert to binary format
c
        BUFF_DA_AXB(J) = A + B*VOLTS(J)
      ENDDO
      RETURN
      END
c
c  End subroutine TRANS_DAC
c
```

```
c*********************************************************************
c*********************************************************************
c
      SUBROUTINE  TRANS_ADC(POWER,NCHANP1,SUM,VA)
c
c  This subroutine converts binary output data to volts using a cali-
c     bration chart by M. Loh, 7/30/89.  The chart may be found in
c     the data aquisition notebook in RM A-32, RCE, MSU.  If the HP
c     power supply is used, the voltage is scaled from approximately
c     10 to 60 volts for heat flux calculations.  (0 to 10 volts is
c     the range for the VaxII/GPX, while the actual voltage output
c     from the power supply is 0 to 60 volts.)
c
      IMPLICIT NONE
c
c  Define integer variables
c
      INTEGER J                 !Dummy variable
      INTEGER NCHANP1           !Total number of channels
      INTEGER POWER             !Indicates use of D/A
c
c  Define real variables
c
      REAL           B             !Slope for volt/binary convr
      REAL           SCALE         !Scaling factor
      REAL           SUM(16)       !Sums for averaging data
      REAL           VA(16)        !Millivolts from A/D
c
c*********************************************************************
c
c  Based on calibration by M. Loh, the voltage was found to vary linear-
c     ly with binary output from 0 to 4095.  The conversion equation
c     is:  volts = B*binary, where B = 0.00243503.
c
      SCALE = 6.52543
      B = 0.00243503
      DO J = 1,NCHANP1
        VA(J) = B*SUM(J)
        IF(J.EQ.NCHANP1.AND.POWER.EQ.1)VA(J) = VA(J)*SCALE
      ENDDO
      RETURN
      END
c
c  End subroutine TRANS_ADC
c
c*********************************************************************
c
c                                  \   __
c@@@@@@@@@@@@@@@@@@@@@@@@@@@@@   ___\ /___\   @@@@@@@@@@@@@@@@@@@@@@@@@@@@@
c........................... /    \|\___/   .............................
c!!!!!!!!!!!!!!!!!!!!!!!!!!! /     /     \   !!!!!!!!!!!!!!!!!!!!!!!!!!!!!!
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c
c
c*********************************************************************
```

APPENDIX C

APPENDIX C

PARAMETER ESTIMATION RESULTS FROM EXPERIMENTAL
REPETITIONS USING CURED COMPOSITE SAMPLES

This appendix contains the results from the estimation of the thermal properties, namely the estimated effective thermal conductivity perpendicular to the fiber axis and the estimated effective density-specific heat product, of the cured $[0°]_{24}$ AS4/EPON 828 composite samples for each repetition with approximate initial temperatures of 25°C, 50°C, 75°C, 100°C, and 125°C in Tables C.1-C.5 respectively. The results for the estimated thermal properties for each repetition of the experiments using cured $[0°, ±30°, ±60°, 90°]_{2(sym)}$ samples with initial temperatures of approximately 25°C, 50°C, and 75°C are given in Tables C.6-C.8, respectively.

Table C.1. Estimated Effective Thermal Conductivity, k, Perpendicular to the Fiber Axis and Density-Specific Heat, ρc, of Cured [0°] AS4/EPON 828-mPDA Composites from Experiments with an Initial Temperature of Approximately 25°C.

Exper. No.[a]	Repet. No.[a]	Temperature Range (°C)	k (W/m°C)	ρc (kJ/m³ °C)	RMS[b] (°C)
1.1	1	26 - 58	0.803	1,590	0.440
	2	26 - 57	0.805	1,580	0.480
	3	26 - 57	0.803	1,570	0.480
	4	32 - 53	0.780	1,580	0.173
	5	35 - 54	0.776	1,590	0.210
	6	26 - 45	0.769	1,570	0.299
	7	30 - 49	0.817	1,590	0.259
	8	30 - 48	0.818	1,550	0.250
	9	30 - 49	0.805	1,600	0.232
1.6	1	27 - 45	0.794	1,590	0.249
	2	29 - 47	0.792	1,550	0.255
	3	29 - 48	0.808	1,540	0.240
	4	25 - 44	0.798	1,590	0.284
	5	25 - 45	0.799	1,590	0.234
	6	25 - 45	0.790	1,580	0.340
1.11	1	26 - 46	0.767	1,560	0.190
	2	26 - 46	0.748	1,560	0.146
	3	27 - 47	0.742	1,580	0.138
	4	26 - 46	0.730	1,560	0.127
	5	26 - 46	0.737	1,550	0.130
	6	26 - 46	0.744	1,540	0.147

a. Experiment and repetition numbers refer to those in Table 4.2.

b. Root mean squared error of calculated versus experimental temperatures.

Table C.2. Estimated Effective Thermal Conductivity, k, Perpendicular to the Fiber Axis and Density-Specific Heat, ρc_p, of Cured [0°] AS4/EPON 828-mPDA Composites from Experiments with an Initial Temperature of Approximately 50°C.

Exper. No.[a]	Repet. No.[a]	Temperature Range (°C)	k (W/m°C)	ρc_p (kJ/m³ °C)	RMS[b] (°C)
1.2	1	52 - 76	0.797	1,650	0.334
	2	53 - 76	0.789	1,640	0.363
	3	52 - 75	0.783	1,670	0.431
	4	54 - 74	0.794	1,620	0.202
	5	54 - 74	0.795	1,650	0.240
	6	54 - 74	0.797	1,660	0.252
1.7	1	50 - 67	0.855	1,700	0.242
	2	50 - 67	0.868	1,660	0.223
	3	50 - 67	0.866	1,660	0.209
	4	50 - 67	0.877	1,740	0.575
	5	50 - 67	0.870	1,740	0.336
	6	50 - 67	0.868	1,680	0.222
	7	52 - 70	0.850	1,620	0.145
	8	52 - 69	0.897	1,670	0.198
	9	49 - 66	0.852	1,680	0.202
	10	50 - 68	0.875	1,640	0.203
	11	51 - 68	0.847	1,640	0.159
	12	51 - 68	0.895	1,710	0.229
1.12	1	52 - 71	0.775	1,620	0.117
	2	52 - 71	0.773	1,620	0.108
	3	53 - 73	0.797	1,610	0.168
	4	53 - 72	0.805	1,620	0.205
	5	52 - 71	0.818	1,550	0.208
	6	52 - 71	0.771	1,610	0.141

a. Experiment and repetition numbers refer to those in Table 4.2.
b. Root mean squared error of calculated versus experimental temperatures.

Table C.3. Estimated Effective Thermal Conductivity, k, Perpendicular to the Fiber Axis and Density-Specific Heat, ρc_p, of Cured [0°] AS4/EPON 828-mPDA Composites from Experiments with an Initial Temperature of Approximately 75°C.

Exper. No.[a]	Repet. No.[a]	Temperature Range (°C)	k (W/m°C)	ρc_p (kJ/m³ °C)	RMS[b] (°C)
1.3	1	78 - 99	0.796	1,670	0.408
	2	78 - 99	0.801	1,680	0.420
	3	76 - 98	0.809	1,680	0.414
	4	78 - 98	0.815	1,720	0.323
	5	78 - 97	0.827	1,710	0.323
	6	78 - 97	0.811	1,700	0.356
1.8	1	75 - 92	0.924	1,830	0.220
	2	75 - 91	0.900	1,820	0.203
	3	75 - 91	0.926	1,760	0.209
	4	75 - 91	0.919	1,820	0.211
	5	75 - 91	0.915	1,830	0.208
	6	75 - 91	0.922	1,820	0.209
1.13	1	77 - 94	0.825	1,780	0.126
	2	75 - 93	0.811	1,740	0.146
	3	77 - 95	0.802	1,760	0.206
	4	77 - 95	0.782	1,770	0.190
	5	77 - 95	0.779	1,760	0.139
	6	77 - 95	0.783	1,760	0.129

a. Experiment and repetition numbers refer to those in Table 4.2.
b. Root mean squared error of calculated versus experimental temperatures.

Table C.4. Estimated Effective Thermal Conductivity, k, Perpendicular to the Fiber Axis and Density-Specific Heat, ρc_p, of Cured [0°] AS4/EPON 828-mPDA Composites from Experiments with an Initial Temperature of Approximately 100°C.

Exper. No.[a]	Repet. No.[a]	Temperature Range (°C)	k (W/m°C)	ρc_p (kJ/m³ °C)	RMS[b] (°C)
1.4	1	102 - 119	0.812	1,780	0.289
	2	102 - 122	0.844	1,910	0.303
	3	102 - 123	0.844	1,900	0.312
	4	102 - 120	0.830	1,980	0.237
	5	102 - 120	0.829	2,020	0.274
	6	102 - 120	0.847	2,000	0.241
	7	101 - 119	0.784	1,850	0.330
	8	103 - 119	0.804	1,830	0.282
	9	103 - 120	0.822	1,840	0.258
	10	102 - 119	0.841	1,830	0.300
	11	102 - 118	0.876	1,910	0.249
	12	102 - 118	0.847	1,950	0.555
1.9	1	100 - 115	0.969	1,950	0.178
	2	100 - 115	0.959	2,000	0.178
	3	100 - 115	0.963	1,930	0.187
	4	100 - 115	0.979	1,960	0.195
	5	100 - 115	0.961	1,960	0.179
	6	100 - 115	0.996	1,970	0.183
1.14	1	100 - 115	0.806	1,850	0.112
	2	100 - 115	0.808	1,850	0.115
	3	100 - 115	0.815	1,850	0.116
	4	100 - 115	0.816	1,810	0.142
	5	100 - 115	0.825	1,850	0.146
	6	100 - 115	0.824	1,790	0.145

a. Experiment and repetition numbers refer to those in Table 4.2.
b. Root mean squared error of calculated versus experimental temperatures.

Table C.5. Estimated Effective Thermal Conductivity, k, Perpendicular to the Fiber Axis and Density-Specific Heat, ρc_p, of Cured [0°] AS4/EPON 828-mPDA Composites from Experiments with an Initial Temperature of Approximately 125°C.

Exper. No.[a]	Repet. No.[a]	Temperature Range (°C)	k (W/m°C)	ρc_p (kJ/m³ °C)	RMS[b] (°C)
1.5	1	126 - 145	0.814	2,150	0.447
	2	126 - 145	0.820	2,220	0.481
	3	126 - 145	0.834	2,170	0.436
	4	127 - 144	0.870	1,980	0.465
	5	127 - 145	0.894	2,000	0.454
	6	127 - 145	0.874	1,940	0.398
	7	128 - 144	0.965	1,960	0.297
	8	128 - 144	0.911	2,000	0.288
	9	128 - 144	0.934	1,990	0.239
1.10	1	126 - 141	1.006	2,070	0.189
	2	126 - 141	0.998	2,130	0.156
	3	126 - 141	1.004	2,110	0.163
	4	126 - 141	1.013	2,110	0.157
	5	126 - 140	1.014	2,090	0.167
	6	126 - 140	1.028	2,050	0.206
1.15	1	126 - 140	0.862	1,990	0.093
	2	126 - 140	0.880	1,910	0.104
	3	126 - 140	0.870	1,930	0.121
	4	126 - 140	0.875	1,920	0.100
	5	126 - 140	0.874	1,940	0.099
	6	126 - 140	0.881	1,920	0.104

a. Experiment and repetition numbers refer to those in Tab. 4.2.

b. Root mean squared error of calculated versus experimental temperatures.

Table C.6. Estimated Effective Thermal Conductivity, k, Perpendicular to the Fiber Axis and Density-Specific Heat, ρc_p, of Cured $[0°,\pm30°,\pm60°,90°]_{2(sym)}$ AS4/EPON 828-mPDA Composites from Experiments with an Initial Temperature of Approximately 25°C.

Exper. No.[a]	Repet. No.[a]	Temperature Range (°C)	k (W/m°C)	ρc_p (kJ/m³ °C)	RMS[b] (°C)
1.16	1	25 - 32	0.697	1,780	0.922
	2	25 - 32	0.690	1,800	0.991
	3	25 - 32	0.667	1,720	0.950
	4	25 - 37	0.660	1,680	0.767
	5	25 - 45	0.685	1,830	0.897
	6	25 - 42	0.648	1,670	0.637
	7	28 - 45	0.716	1,680	0.166
	8	28 - 45	0.727	1,680	0.168
	9	28 - 49	0.659	1,520	0.176
	10	29 - 49	0.696	1,560	0.183
	11	29 - 48	0.713	1,590	0.200
1.19	1	26 - 49	0.716	1,540	0.246
	2	29 - 53	0.754	1,610	0.194
	3	25 - 48	0.765	1,610	0.268
	4	25 - 49	0.750	1,610	0.250
	5	31 - 55	0.813	1,640	0.247
	6	30 - 53	0.800	1,630	0.206

a. Experiment and repetition numbers refer to those in Table 4.2.
b. Root mean squared error of calculated versus experimental temperatures.

Table C.7. Estimated Effective Thermal Conductivity, k, Perpendicular to the Fiber Axis and Density-Specific Heat, ρc_p, of Cured $[0°,\pm30°,\pm60°,90°]_{2(sym)}$ AS4/EPON 828-mPDA Composites from Experiments with an Initial Temperature of Approximately 50°C.

Exper. No.[a]	Repet. No.[a]	Temperature Range (°C)	k (W/m°C)	ρc_p (kJ/m³ °C)	RMS[b] (°C)
1.17	1	52 - 76	0.723	1,660	0.134
	2	53 - 76	0.708	1,640	0.183
	3	52 - 75	0.709	1,620	0.176
	4	54 - 74	0.724	1,650	0.302
	5	54 - 74	0.726	1,630	0.165
	6	54 - 74	0.709	1,690	0.413
1.20	1	50 - 67	0.809	1,710	0.326
	2	50 - 67	0.802	1,700	0.383
	3	50 - 67	0.805	1,700	0.352
	4	50 - 67	0.767	1,680	0.403
	5	50 - 67	0.766	1,680	0.353
	6	50 - 67	0.766	1,640	0.222

a. Experiment and repetition numbers refer to those in Table 4.2.
b. Root mean squared error of calculated versus experimental temperatures.

Table C.8. Estimated Effective Thermal Conductivity, k, Perpendicular to the Fiber Axis and Density-Specific Heat, ρc_p, of Cured $[0°,\pm30°,\pm60°,90°]_{2 (sym)}$ AS4/EPON 828-mPDA Composites from Experiments with an Initial Temperature of Approximately 75°C.

Exper. No.[a]	Repet. No.	Temperature Range (°C)	k (W/m°C)	ρc_p (kJ/m³ °C)	RMS[b] (°C)
1.18	1	78 - 96	0.735	1,740	0.151
	2	78 - 96	0.743	1,730	0.153
	3	78 - 97	0.738	1,730	0.177
	4	78 - 96	0.747	1,700	0.155
	5	78 - 97	0.759	1,680	0.194
	6	78 - 97	0.745	1,720	0.151
1.21	1	76 - 98	0.721	1,750	0.415
	2	77 - 96	0.884	2,240	0.623
	3	76 - 97	0.757	1,720	0.490
	4	76 - 96	0.744	1,740	0.423
	5	76 - 97	0.748	1,740	0.432
	6	76 - 97	0.749	1,730	0.426

a. Experiment and repetition numbers refer to those in Table 4.2.

b. Root mean squared error of calculated versus experimental temperatures.

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