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By

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Abstract

ESTIMATION OF THE KINETIC PARAMETERS OF AN AMINE-EPOXY RESIN DURING CURE

By

Zoubeir Saad

Thermoset resins are an important component in advanced composite materials, and the curing process is a critical phase in the fabrication of these materials. The objectives of this study were to investigate and compare the use of Differential Scanning Calorimetry (DSC) and dielectrometry data for the estimation of the kinetic parameters associated with three kinetic models used to describe the curing of an amine-epoxy thermoset resin using both the linear regression and Box-Kanemasu estimation methods. The results of the estimation procedure indicated that the kinetic models which include autocatalyzation were better suited in describing the kinetic reactions than one solely based on nth order kinetics. In addition, the use of DSC data resulted in parameter estimates with less variability than the use of dielectric data, and the use of the Box-Kanemasu method generally provided less variability in the parameter estimates than those resulting from the use of the linear regression method.

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Nomenclature

a_1	Primary amine
a_2	secondary amine
a_3	tertiary amine
A_1, A_2	Pre-exponential constants
b	Estimated parameter vector
B	Initial ratio of the amine equivalents to the epoxide equivalents
E_1, E_2	Activation energy constants (kJ/mole)
h	Scalar interpolation factor
HX_o, HX_a	Hydroxyls
K_1, K_2	Reaction rate constants
m	Exponential constant in kinetic models
n	Exponential constant in kinetic models
N	Number of observations
p	Number of parameters to be estimated
q(t)	Heat generated by the chemical reaction at time t
Q_o	Total heat of reaction
R	Gas constant

S	Sum of the squares function
t	Time
t_f	Time required to complete a 100% cure
T	Absolute temperature
$\mathbf{U}$	Weighting matrix [p×p]
$\mathbf{W}$	Weighting matrix [n×n]
$\mathbf{X}$	Sensitivity coefficient matrix
Y_o	Observed value
Y_p	Predicted value
$\mathbf{Y}_o$	Observation vector
$\mathbf{Y}_p$	Predicted vector
α	Degree of cure
β	Parameter vector [p×1]
ε_o	Permitivity of free space
ε_r	"Relaxed" permitivity
ε_u	"Unrelaxed" permitivity
ε'	Relative permitivity
ε''	Loss factor
σ	Ionic conductivity
σ_i	Conductivity at 0% cure
σ_f	Conductivity at 100% cure
σ^2	Variance

ρ	Resistivity
τ_d	Dipole relaxation time

Chapter 1

Introduction

Thermoset resins are important compounds in the formation of fiber reinforced composite materials, high performance coatings, and adhesives. The use of high performance fiber reinforced composite materials in particular has been expanding for at least two decades in many sectors of industry, particularly in the aerospace, automotive and sporting goods sectors. Consequently, there has been an increased focus and attention on thermoset resins by researchers due to the increased use of thermoset advanced composites. The most important facet of processing matrix resins is the curing procedure in which chemical reactions prompt the structural changes within the resin and bind the matrix to the reinforcing fibers. The understanding of the curing reactions of thermoset resins and the development of a reliable method to monitor them are important in producing a consistent and high quality material.

The purpose of this research is to investigate the cure of a thermoset epoxy/amine resin. This study consists of experimental and theoretical components for the estimation of the kinetic parameters associated with several kinetic models proposed in the literature to describe the curing process.

The experimental portion of this investigation involves the monitoring of the curing process using two different techniques: Differential Scanning Calorimetry (DSC) and dielectrometry. In DSC experiments, the input power difference between the sample holder and a reference container maintained at the same temperature is monitored. This difference is proportional to the rate of cure, and the constant of proportionality is the

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The experimental portion of this investigation involves the monitoring of the curing process using two different techniques: Differential Scanning Calorimetry (DSC) and dielectrometry. In DSC experiments, the input power difference between the sample holder and a reference container maintained at the same temperature is monitored. This difference is proportional to the rate of cure, and the constant of proportionality is the total heat released during cure. In dielectrometry experiments, the dielectric properties of the epoxy are measured by the microdielectrometer by applying a voltage across the sample using two conducting electrodes. The dielectric measurements are related to the degree of cure of the epoxy at a given time using log conductivity data.

The second part of the study is focused on the estimation of the cure kinetic parameters associated with an appropriate kinetic mathematical model from both DSC and dielectric data. Two different estimation methods were employed: the linear regression method and the Box-Kanemasu estimation method. The linear regression method minimizes the sum of the differences between the expected value and the measured values of a function. In utilizing this method, the function is assumed to be linear with the dependent variable. This method has been used by other researchers (Sourour et al. (1976), Scott (1989)) for the estimation of kinetic parameters associated with the curing of thermoset resins. In utilizing this procedure, researchers often "force" the kinetic model, which is actually in the form of a differential equation, into a linear function. A different method, called the Box-Kanemasu Method, is proposed for use in analyzing the cure kinetics in this study. It is a modification of the Gauss minimization method which can be used for nonlinear models. This method was modified to treat the differential equation associated with the curing models under consideration. This is the first attempt to estimate the parameters associated with the curing of a thermoset resin using this method.

The objective of this research is to compare the two experimental methods and the two estimation procedures discussed previously for the estimation of kinetic properties associated with three kinetic models for a thermoset resin during cure. The thermoset under investigation is an amine-epoxy resin.

Chapter 2

Literature Review

2.1 Kinetics of Reactions of Amine Epoxy Resins:

It has been proven that the hardening of epoxide resins with amines involves many complex chemical reactions. Researchers have studied this complicated process over the last four decades in order to determine its true chemistry and develop a relatively easy mathematical model to describe the curing process of these resins.

Shechter et al. (1956) and Smith (1961) found that the two major compounds which react with the epoxide are the primary and secondary amines. The principal reaction is the reaction of a primary amine with the epoxide to form a secondary amine. The secondary amine subsequently reacts with the epoxide to form a tertiary amine. These two reactions were proven to be accelerated by the presence of a compound capable of acting as a hydrogen-bond donor (e.g., alcohols, phenols, acids and amides). Shechter et al. (1956) reported that the epoxy-amine reactions are catalyzed by hydroxyls in the early stages and become autocatalyzed as the curing process progresses.

Later studies by Horie et al. (1970), Bokare et al. (1979) and Barton (1985) were consistent with the early researchers. They proposed the following set of reactions to describe the mechanism of the curing of epoxide resins with amines:

$$a_1 + E + HX_A \xrightarrow{K_1} a_2 + HX_A$$

$$a_1 + E + HX_O \xrightarrow{K_1'} a_2 + HX_O$$

$$a_2 + E + HX_A \xrightarrow{K_2} a_3 + HX_A$$

$$a_2 + E + HX_O \xrightarrow{K_2'} a_3 + HX_O$$

In these reactions a_1, a_2 and a_3 are the primary, secondary, and tertiary amines, and E is the epoxide. The hydroxyl, HX_O, exists in the system as impurity, and the hydroxyl, HX_A, is formed by the reaction of the amine with the epoxide. The reaction rate constants, K_1, K_1', K_2 and K_2', can be functions of temperature and the physical state of the reaction. Barton (1985) noted that the hydroxyl formed (HX_A) is an active catalyst; this explains the acceleration of the reaction in the early stages of the cure which is typical of an autocatalytic reaction. Chern et al. (1987) also indicated that the curing process is stimulated by added hydrogen-bond donor solvent and hydroxyl groups created in the process. They added that a reaction of etherification is possible in the process with an excess of epoxide, but that it is negligible in the case of an excess of amine.

Many researchers have formulated relatively simple mathematical models to describe the kinetics of the curing mechanism. Basically, all the implemented formulas relate the rate of consumption of the epoxide to other independent variables such as time and temperature. Barton (1985) presented, for a given temperature, the general form for the kinetic models of the curing of amine-epoxide resins as

$$\frac{d\alpha}{dt} = K \times f(\alpha) \tag{2.1}$$

where $f(\alpha)$ is a function of the fractional conversion (or degree of cure) α, and $d\alpha/dt$ is the rate of the conversion. The rate constant, K, is usually assumed to be a function of the temperature with the Arrhenius form:

$$K = A\exp\left(-\frac{E}{RT}\right) \tag{2.2}$$

where A is a constant, R is the gas constant, E is the activation energy, and T is absolute temperature. Barton (1985) also suggested that the reaction kinetics of an nth order involving only one reacting substance could be described by the equation implemented by Prime (1973):

$$\frac{d\alpha}{dt} = K(1-\alpha)^n \tag{2.3}$$

where K is again the apparent rate constant which is assumed to follow an Arrhenius relationship with temperature (eq.(2.2)).

Kamal et al. (1973), Ryan et al. (1979), and Hagnauer et al. (1983) assumed a different expression for the curing of the epoxy resins. In this case, an empirical expression was developed:

$$\frac{d\alpha}{dt} = (K_1 + K_2\alpha^m)(1-\alpha)^n \tag{2.4}$$

where m and n are constants independent of the temperature, and K_1 and K_2 are rate constants which are assumed to follow the Arrhenius relationship with temperature (eq.(2.2)).

A slightly different model from eq. (2.4) was proposed by Sourour and Kamel (1976). The following equation that was suggested takes in account the ratio of the amine equivalents to the epoxide equivalents:

$$\frac{d\alpha}{dt} = (K_1 + K_2\alpha)(1-\alpha)(B-\alpha) \tag{2.5}$$

where B is the initial ratio of the amine equivalents to the epoxide equivalents. However,

in the case of a reaction with stoichiometric quantities of the reactants (epoxide and amine), the value for B is equal to 1. The kinetic equation becomes

$$\frac{d\alpha}{dt}=(K_1+K_2\alpha)(1-\alpha)^2 \tag{2.6}$$

Sourour and Kamel (1976) also suggested that the cure reactions that are purely autocatalyzed can be described as

$$\frac{d\alpha}{dt}=K\alpha(1-\alpha)^2 \tag{2.7}$$

Likewise, cure reactions that are not autocatalyzed can be described by this equation

$$\frac{d\alpha}{dt}=K(1-\alpha)^2 \tag{2.8}$$

Sichina also suggested that the autocatalyzed curing reactions can be formulated by

$$\frac{d\alpha}{dt}=K\alpha^m(1-\alpha)^n \tag{2.9}$$

Most of the mentioned researchers have agreed that the curing reactions of resins initially are controlled by chemical kinetics. However, as the epoxy hardens the process becomes diffusion controlled in the latter stages of the cure. Therefore, the equations that were presented (eq.(2.1) through eq.(2.11)) are intended to describe the kinetics for the first portion of the curing process ($\alpha<\approx0.5$). The number of different kinetic models proposed by different researchers is an indication of the difficulty of characterizing the curing reaction, even for only the initial portion of the cure. None of the models proposed above is capable of completely describing the actual kinetic reactions, and it is often difficult to select the appropriate model.

2.2 Experimental Methods Utilized with Amine Epoxy Resins:

2.2.1 Differential Scanning Calorimetry (DSC):

Differential Scanning Calorimetry or DSC has been known and employed by many researchers since its introduction as a commercial instrument during the 1960's. It has been also certified by the Nomenclature Committee of International Confederation for Thermal Analysis (ICTA) as a valid technique for monitoring exothermic reactions. The main notion of this expertise (DSC) is that the energy flow to the reacting substance is proportional to the reaction rate.

There are two types of differential scanning calorimeters: one which operates using the heat flux mode and one which operates using the power compensation mode. Each of these methods has a different basis for measurements, as described by Mackenzie (1979).

The heat flux DSC is a modified Differential Thermal Analysis (DTA) instrument which has the sample and the reference in different holders connected by a controlled thermal resistance and external thermocouples. Boersma (1955) showed that the difference between temperature of the sample holder and the reference holder can be related to the heat flux; this is the basis of measurements for the heat flux DSC (Barton, 1985). In this DSC, the temperature difference is measured and used to determine the heat flux.

The power compensation DSC was first described by Watson et al. (1964) and by O'Neill (1964), and it was developed into a commercial instrument by the Perkin-Elmer Corporation (Barton 1985). This type of DSC, which was used in this research work, employs different sample and reference containers which have very low thermal masses.

2.2 Experimental M[illegible]

2.2.1 Differential [illegible]

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The [illegible] which has the [illegible] a controlled thermal [illegible] that the difference between [illegible] reference holder can be related to the heat [illegible] the heat flux DSC (Barton, 1985). In this DSC the temperature difference is measured and used to determine the heat flux.

The power compensation DSC was first described by Watson et al. (1964) and by O'Neill (1964), and it was developed into a commercial instrument by the Perkin-Elmer Corporation (Barton 1985). This type of DSC, which was used in this research work employs different sample and reference containers which have very low thermal masses.

Each of these two containers has its own heater and platinum thermometer. This system has an internal control loop that varies the power supplies to the heaters of each container in order to minimize the temperature difference recorded by the temperature sensors (Barton (1985)). This second type of DSC measures the power required to keep the temperature of the sample and the temperature of the reference identical.

Lee et al. (1981), Dallek et al. (1982), and Hohne et al. (1983) indicated that the these two types of DSC's accomplish the similar performance in the monitoring of the heat flow during exothermal reactions. Nielsen (1974) noted that the small size of the sample is required to minimize the temperature gradient across the sample. Good thermal contact between the sample, the container, and the heater is also required to reduce heat losses.

2.2.2 Dielectric Analysis:

Dielectric measurements have been used since 1934 when Kienle and Race (1934) first reported the use of the dielectric analysis to examine polyestrification reactions. Until the late 1950's, the literature is sparse. Then, at the beginning of the 1960's, thermoset polymers became more significant, and instrumentation and equipment for measurement began to emerge. However, there is still very little information to be found in the literature related to the use of dielectric measurements for the characterization of curing in thermoset resins.

Dielectric measurements are accomplished by applying a voltage across a sample of material using two conducting electrodes. Consequently, the sample becomes electrically polarized (dielectric response) and/or conducts net charges. These two phenomena induce currents inside the material which can vary significantly during the

curing process.

The first effort to describe the kinetics of the composite curing process using dielectric data was done by Warfield and Petree (1959 and 1960). They investigated the relationship between the log of resistivity ρ, which is a dielectric parameter, and the degree of cure at different temperatures using diallyl phthalate and epoxy amine resins. Kagan et al. (1968) used Warfield 's relationship between the log resistivity and the degree of cure α. Kagan modeled the kinetic of the curing process based on the assumption of proportionality between α and log(ρ). He obtained the empirical constants and the activation energies from his data but did not compare them with other methods. A similar attempt was done by Acitelli et al. (1971) to relate the log resistivity to the degree of cure using bisphenol-A-diglycidyl ether (BADGE) cured with m-phenylene diamine (MPDA). Acitelli also used DSC and IR data to compare with his resistivity data. He found the same empirical constants from all the methods he used. Day (1987) conveyed that during an isothermal cure, the log resistivity is related to the degree of cure and that relationship can only hold over a limited degree of reaction. He speculated that this relationship could be linear.

2.3 Estimation of Cure Kinetic Parameters:

2.3.1 Linear Regression Method:

Linear regression is a statistical tool that inspects the relationship between a dependent variable Y and an independent variable X. The dependent variable is assumed to behave as a linear function of the independent variable.

$$Y=C_0+C_1X \tag{2.10}$$

where C_1 and C_2 are constants.

curing process.

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2.3 Estimation [illegible]

2.3.1 Linear Regression [illegible]

Linear regression is a statistical tool that inspects the relationship between a dependent variable Y and an independent variable X. The dependent variable is assumed to behave as a linear function of the independent variable

$$Y=C_1+C_2X \tag{2.10}$$

where C_1 and C_2 are constants.

The differences between the predicted values and the observed values are called residuals. The regression method is based on the minimization of the sum of the squared residuals, for which the constants C_1 and C_2 are calculated. In order to evaluate the adequacy of the model one has to analyze the residuals and compare them with the values of the independent variable.

$$S=\sum_{1}^{n}(Y_{o,i}-Y_{p,i})^2=\sum_{1}^{n}(Y_{o,i}-C_0-C_1X_i)^2 \tag{2.11}$$

where Y_o is the observed value, Y_p is the predicted value and n is the number of observations.

The linear regression method has been used by many researchers to estimate the kinetic parameters due to its simplicity and flexibility to different models. The kinetic model is usually rearranged in order to have a function with a linear variation with the degree of cure α. Sourour and Kamal (1976) called this function the reduced reaction rate. Other researchers used this method to estimate kinetic exponents. For instance, the rate constant K and the exponential n in eq. (2.3) can be estimated by taking the logarithm of this equation and then estimating log K and n using the linear regression method.

2.3.2 Box-Kanemasu Interpolation Method:

This method is a modification of the Gauss minimization method. The main scheme of this method is to minimize the sum of squares function S.

$$S=[Y-\eta(\beta)]^{T}W[Y-\eta(\beta)]+(\mu-\beta)^{T}U(\mu-\beta) \tag{2.12}$$

where Y is the observation vector [n×1], η is the model vector [n×1], β is the parameter vector [p×1], μ is the parameter vector from prior information [p×1], W and U are weighting matrices with the dimensions respectively [n×n] and [p×p].

Beck and Arnold (1977) indicated that the Gauss method is a relatively simple and practical method in cases of well-defined minima provided the initial estimates are in the neighborhood of the minimum. Box and Kanemasu (1972) also explained that the Gauss method does not always lead to convergence in the case of poor initial guesses for the parameters or severe non-linearity of the model. They added that, in this case, large oscillations could occur from one iteration to another leading to instability in the estimation process. In order to improve the Gauss estimation method, Box and Kanemasu (1972) suggested a small correction in the direction proposed by Gauss. They also did not include a check that the sum of squares decreases from one iteration to another in order to reduce the number of calculations (Beck and Arnold (1977)).

Chapter 3

Theoretical Analysis

3.1 Kinetics of Reactions:

Due to the complexity of the curing process of epoxide resins, several assumptions were employed with the suggested mathematical models to describe the kinetics of the reactions of this mechanism. It is assumed that the curing process consists of two stages: 1. the stage that is controlled by the chemical kinetics (degree of cure is less than approximately 50%) which will be investigated in this research work; and, 2. the diffusion controlled stage (degree of cure is greater than approximately 50%).

Three models were investigated to describe the curing process in the initial stage ($\alpha < \approx 50\%$). The equations were presented previously by eq. (2.4), (2.6) and (2.3) and written below

$$\textit{Model 1:} \quad \frac{d\alpha}{dt} = (K_1 + K_2\alpha^m)(1-\alpha)^n \qquad \text{m=n=1} \tag{3.1}$$

$$\textit{Model 2:} \quad \frac{d\alpha}{dt} = (K_1 + K_2\alpha)(1-\alpha)^2 \tag{3.2}$$

$$\textit{Model 3:} \quad \frac{d\alpha}{dt} = K_1(1-\alpha)^n \tag{3.3}$$

where K_1 and K_2 follow the Arrhenius relationship with the absolute temperature as previously explained by eq. (2.2):

$$K_i = A_i \exp\left(-\frac{E_i}{RT}\right) \qquad i=1,2 \qquad (3.4)$$

The first two models described in eqs. (3.2) and (3.3) are based on the assumption that the process is an autocatalyzed reaction. Furthermore, if the exponents m and n are equal to one in the first model, a second order reaction is assumed since the sum of the exponents is equal to two. However, in order to use the third model (eq.(3.1)), one has to assume that the curing process is an nth order reaction with no autocatalyzation.

These models will be analyzed using two experimental procedures: Differential Scanning Calorimetry (DSC) and dielectric analysis. The Arrhenius constants, E_i and A_i, associated with the rate constants, K_i, and the exponential, n, in the third model are the parameters to be estimated.

3.2 Analysis of the Curing Procedures:

3.2.1 Differential Scanning Calorimetry (DSC):

This method is based on the assumption that the heat flow of the reaction is proportional to the reaction rate as indicated by

$$\frac{d\alpha}{dt} = \frac{1}{Q_o}\frac{dq}{dt} \qquad (3.5)$$

where q(t) is the heat generated by the chemical reaction at time t and Q_o is the total heat of reaction. The total heat of reaction is found from

$$Q_o=\int_0^{t_f}\left(\frac{dq(t)}{dt}\right)_d dt \tag{3.6}$$

where $(dq(t)/dt)_d$ is the instantaneous rate of heat generated during a dynamic scanning and t_f is the time required to complete a 100% cure. A dynamic scan is one in which the temperature is increased linearly with time.

3.2.2 Dielectric Analysis:

The dielectric response of a material involves a capacitive nature which is its ability to store charges. It also consists of a conductive nature which is its capability to pass charges from one side to the other. The measurement of the dielectric responses of a material is conducted by placing a piece of the material between two conducting electrodes, applying a time varying voltage and measuring the outcoming current. Due to the voltage applied between the two electrodes, the material becomes electrically polarized (capacitive nature) and pass charges from one electrode to the other (conductive nature). These two factors induce, through the material, a current which changes enormously during the curing process.

Five microscopic phenomena contribute significantly in the dielectric response of a composite material (Stephen et al. (1985)). The first phenomenon is the ionic conductivity which is the passage of ions through the material due to the electric field inside the material. Dipoles are the second phenomenon that affect the dielectric response; there are two different dipole classifications: 1. induced dipoles which are caused by the separation of the charges on nonpolar bonds due the presence of the electric field; and, 2. static dipoles which require molecular motion to orient. Induced dipoles are independent of frequency because they react very quickly. On the other

hand, static dipoles are frequency dependent; their orientation in an electric field is usually described by a decay function of the form $e^{(-t/\tau)}$ with τ_d as the relaxation time. The third phenomenon of the dielectric response is the electrode polarization which is characterized by a capacitive effect caused by the build-up of charges at the interface of the material with the electrodes. This phenomenon is usually caused by a high ionic conduction level. Electronic conduction is the fourth phenomenon that affects the dielectric response of a material, it is usually very insignificant in common composite materials. The effect of Maxwell-Wagner inhomogeneities is the last phenomenon. It is a combination of the four previous phenomena due to the mixture of different materials with different dielectric properties.

The ionic conductivity and dipoles are the most important phenomena related to the dielectric properties of polymers. The ionic conductivity is of particular interest in the characterization of the curing reactions as it is directly related to the viscosity of the resin before gelatinization. The viscosity is an indication of the degree of cure; therefore, the curing reactions can be analyzed from ionic conductivity data.

The two dielectric parameters that can be measured are the relative permitivity, ε', and the loss factor, ε''. Each of these two parameters is affected by the dipoles and the ion conductivity phenomenon. The loss factor can be related to the ionic conductivity, σ, of the thermoset (Stephen et al., 1985):

$$\varepsilon''=\frac{\sigma}{\omega\varepsilon_o}+\frac{(\varepsilon_r-\varepsilon_u)\omega\tau_d}{1+(\omega\tau_d)^2} \tag{3.7}$$

where ω is the angular frequency of the voltage, ε_o is the permitivity of free space, ε_u is the "unrelaxed" permitivity which is equivalent to the baseline permitivity (ε_∞), ε_r is the "relaxed" permitivity when molecular dipoles align with the electric field at the

maximum, and τ_d is the dipole relaxation time. The first term on the right hand side of eq. (3.7) is the conductivity term and the second one characterizes the dipole effect.

In order to extract the conductivity one has to multiply the eq. (3.7) by $\varepsilon_o\omega$:

$$\varepsilon''\varepsilon_o\omega=\sigma+((\varepsilon_r-\varepsilon_u)\omega\tau)/(1+(\omega\tau)^2) \tag{3.8}$$

Different frequencies are used for the voltage applied across the sample. By plotting $\varepsilon''\varepsilon_o\omega$ as a function of time for each of the frequencies, regions of superpositions appear from the different frequency curves. These regions of superposition are the ionic conductivities of the material since they are independent of the frequency. In the case when superposition does not occur between the curves of the different frequencies, the curve of the lowest frequency was always selected to be equal to the conductivity σ since $((\varepsilon_r-\varepsilon_u)\omega\tau_d\varepsilon_o\omega)/(1-(\omega\tau_d)^2)$ is small for low frequencies.

Once the conductivity of the sample is computed at a given curing time, then the degree of cure α can be calculated assuming a linear relationship between α and log(σ):

$$\alpha=\frac{\log(\sigma_f)-\log(\sigma)}{\log(\sigma_f)-\log(\sigma_i)} \tag{3.9}$$

where σ is the instantaneous conductivity of the sample during cure, σ_f is the conductivity at 100% cure and σ_i is the conductivity at 0% cure. The conductivity at the 100% cure was obtained from a dynamic dielectric scan starting from ambient temperature at time t=0 until no evidence of further reactions; the final conductivity value was selected as the conductivity at 100% cure.

3.3 Estimation of the Kinetic Parameters:

3.3.1 Regression Method:

This method is based on the assumption that the dependent variable Y behaves as a linear function of the independent variable X. Then, the slope and the intercept of this function are estimated by minimizing the sum of the squared differences between the measured values of the dependent variable (Y_o) and the predicted ones (Y_p):

$$S=\sum_{1}^{m}(Y_{o,i}-Y_{p,i})^2 \tag{3.10}$$

where $Y_{p,i}=C_o+C_1X_i$. In order to minimize S, eq. (3.13) is differentiated with respect to the two parameters C_o and C_1, and the resulting expressions are set equal to zero. These equations are then solved for C_o and C_1:

$$C_o=\frac{(\sum Y_{o,i})(\sum X_i^2)-(\sum X_i)(\sum Y_{o,i}X_i)}{n\sum X_i^2-(\sum X_i)^2} \tag{3.11}$$

$$C_1=\frac{n\sum Y_iX_i-(\sum X_i)(\sum Y_i)}{n\sum X_i^2-(\sum X_i)^2} \tag{3.12}$$

In order to use this method for the estimation of the parameters of the first and second kinetic models (eq. (3.1) and eq. (3.2)), the equations are rearranged as follows:

$$\frac{d\alpha/dt}{(1-\alpha)^i}=K_1+K_2\alpha \qquad i=1,2 \tag{3.13}$$

where the left hand side of the equation is assumed to be the dependent variable and α is the independent variable. In the third model, the logarithm of $d\alpha/dt$ is assumed to be the dependent variable and the logarithm of $(1-\alpha)$ is assumed to be independent

variable:

$$\ln(d\alpha/dt)=\ln(K_1)+n\ \ln(1-\alpha) \tag{3.14}$$

where $\log(K_1)$ and n are the parameters to be estimated. Note that in each of these cases, α and/or $d\alpha/dt$ appears in the expression for the dependent variable, and the parameters estimated are constants. As stated previously, the rate constants K_1 and K_2 are assumed to follow the Arrhenius relationship with absolute temperature. Therefore, the parameters K_1 and K_2 are estimated from isothermal experiments.

The pre-exponential constants, A_i, and the activation energies, E_i, are estimated from the Arrhenius expression in eq. (3.4) again using linear regression. In this case, the logarithm of the rate constants ($\ln(K_1)$ and $\ln(K_2)$) are the dependent variables, 1/RT is the independent variable, and $\ln(A_i)$ and E_i are the parameters to be estimated:

$$\ln(K_i)=\ln(A_i)-E_i(1/RT) \qquad i=1 \text{ or } 2 \tag{3.15}$$

In the estimation procedure, the values of $\ln(A_i)$ are determined from estimates of K_i obtained from a number of isothermal experiments conducted at several different temperatures.

3.3.2 Box-Kanemasu Interpolation Method:

This method is a modification of the Gauss method which is described by Beck and Arnold (1977) as being simple and a very effective method of minimization for nonlinear models. This method minimizes the sum of squares function S:

$$\boldsymbol{S}=[\boldsymbol{Y}_o-\boldsymbol{Y}_p]^T[\boldsymbol{Y}_o-\boldsymbol{Y}_p] \tag{3.16}$$

Note that eq. (3.16) is in the same form as eq. (3.10); however, in this case the predicted

vector Y_p is not limited to a linear model. Instead, it contains calculated values corresponding to the measured values in Y_o, the observation vector. For example, if the dielectric data is used, Y_o contains measured values of α, and Y_p contains calculated values of α obtained from the solution of the differential kinetic model.

In order to minimize S, eq. (3.16) is differentiated with respect to the unknown kinetic parameters, and the resulting expression is set equal to zero.

$$\nabla_\beta S=2[-X(\beta)][Y_o-Y_p(\beta)]=0 \qquad (3.17)$$

where β contains the true parameter values, and $X(\beta)$ is the sensitivity coefficient matrix which is defined as $[\nabla_\beta Y_p^T(\beta)]^T$.

Since the kinetic models that were presented earlier are not linear, it is not possible to solve explicitly for the parameter vector β. In order to avoid this non-explicit problem an estimate for the parameter vector must be proposed. Two approximations must be used to transform this equation into an iterative form: 1. $X(\mathbf{b})$ is used as an approximation for $X(\beta)$, where $\mathbf{b}$ is the estimate of β, and, 2. $Y_p(\beta)$ is approximated using the first two terms of a Taylor series for $Y_p(\beta)$ about $\mathbf{b}$. The resulting expression is:

$$X^T(b)[Y_o-Y_p(\beta)-X(b)(\beta-b)]\approx 0 \qquad (3.18)$$

The parameter vector can then be computed as:

$$\beta=b+P(b)[X^T(b)(Y_o-Y_p(b))] \qquad (3.19)$$

where $P(\mathbf{b})$ is a vector such as $P^{-1}(\mathbf{b})=X(\mathbf{b})^TX(\mathbf{b})$.

It has been proven that the calculated value β would be a better estimate than the previous estimate $\mathbf{b}$ if the model is not very far from being linear in the region including β and $\mathbf{b}$. An iterative format of eq. (3.19) is represented as follows: (Beck and Arnold, 1977).

$$b^{(k+1)}=b^{(k)}+h^{(k+1)}\Delta_g b^{(k)} \tag{3.20}$$

$$\nabla_g b^{(k)}=P^{(k)}[X^{T(k)}(Y_o-Y_p^{(k)})] \tag{3.21}$$

where the superscript k is the iteration number, and $h^{(k+1)}$ is a scalar interpolation factor.

In the Box-Kanemasu method, S is estimated at each iteration as a second order polynomial function of the scalar interpolation factor h. The value of $h^{(k+1)}$ is calculated by minimizing the estimated function S (Beck and Arnold, 1977).

$$h^{(k+1)}=G^{(k)}[S_1^{(k)}-S_o^{(k)}+2G^{(k)}]^{-1} \tag{3.22}$$

where $G_{(k)}$ is defined by $[\Delta_g \mathbf{b}^{(k)}]^T \mathbf{P}^{-1(k)} \Delta_g \mathbf{b}^{(k)}$, S_0 and S_1 are the value of S for h equal to 0 and 1 respectively. The value of $h^{(k+1)}$, then, is used to calculate the estimated values of the parameters at the (k+1)st iteration. A modification of the flow chart presented by Beck and Arnold (1977) is presented in Figure 3.1 to illustrate the Box-Kanemasu estimation procedure.

The Box-Kanemasu method is incapable of estimating the parameters in the case of a correlation (linear dependency) between the sensitivity coefficients due to the fact that the sum of the squares function does not have a unique minimum. It has been proven that even in the case of near linear dependency between the sensitivity coefficients trouble could be encountered in convergence (Beck and Arnold, 1977). For reliable estimation results, the sensitivity coefficients must be plotted and examined for possible correlation. In the case of a single response and a constant standard deviation, it is advised to examine:

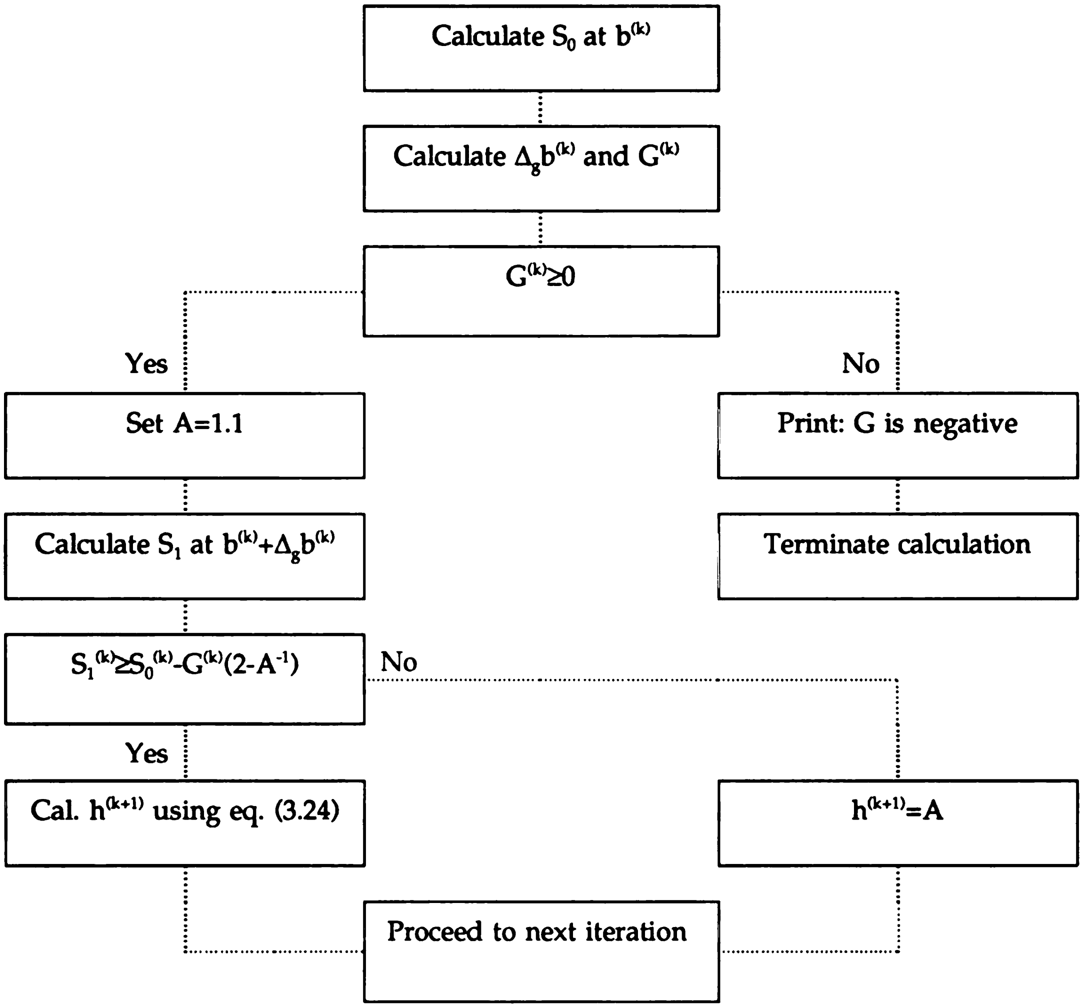

Figure 3.1 Flow Chart for the Box-Kanemasu Estimation Procedure

$$X'_i=\beta_i X_i=\beta_i \frac{\partial Y_p}{\partial \beta_i} \tag{3.23}$$

Since the DSC system measures the rate of cure of the thermoset resin, it was necessary to use the rate of cure vector as the observation vector, and subsequently, the sensitivity coefficients were calculated with respect to the rate of cure. For example, the sensitivity coefficients associated with Model 1 are:

$$X'_1=\frac{d}{dt}\left(K_1\frac{\partial\alpha}{\partial K_1}\right)=K_1(1-\alpha)+K_1[K_2(1-2\alpha)-K_1]\frac{\partial\alpha}{\partial K_1} \tag{3.24}$$

$$X'_2=\frac{d}{dt}\left(K_2\frac{\partial\alpha}{\partial K_2}\right)=K_2\alpha(1-\alpha)+K_2[K_2(1-2\alpha)-K_1]\frac{\partial\alpha}{\partial K_2} \tag{3.25}$$

Contrarily, the dielectric system measures the degree of cure directly. In this case, the degree of cure was the observation parameter and the sensitivity coefficients were calculated with respect to the degree of cure α. The dielectric analysis then required an explicit formulation of the degree of cure as a function of time, K_1, and K_2 in the isothermal case, or as a function of time, temperature, A_1, and E_1 in the non-isothermal case. Each of the differential equations of the kinetic models was solved using the initial condition, $\alpha=0$ at $t=0$. Then, the sensitivity coefficients were computed using finite differences as shown below:

$$\frac{\partial\alpha}{\partial K_1}\approx\frac{\alpha(K_1+\delta K_1)-\alpha(K_1)}{\delta K_1} \tag{3.26}$$

$$\frac{\partial\alpha}{\partial K_2} \approx \frac{\alpha(K_2+\delta K_2)-\alpha(K_2)}{\delta K_2} \tag{3.27}$$

The sensitivity coefficients were computed, plotted, and examined for each of the three models for the DSC and the dielectric case. Correlation (or even near correlation) between sensitivity coefficients is an indication that either the number of parameters must be reduced or that the model must be modified.

The confidence regions for each estimated parameter b_i can be approximated as indicated below:

$$b_i \pm \left(P_{ii}\frac{S}{(N-p)}\right)^{1/2} t_{1-\alpha/2}(N-p) \qquad i=1,2,\ldots,p \tag{3.28}$$

with p is the number of parameters to be estimated, N is the number of the data points collected, P_{ii} is the ith diagonal term of the P matrix (eq.(3.19)) and it represents the variance of the parameter b_i, S is the sum of the squared residuals and $t_{1-\alpha/2}(N-p)$ is the value of the t distribution function for $(1-\alpha/2)$ confidence region and (N-p) degrees of freedom.

This expression for the confidence interval for the parameter b_i is an approximation provided for nonlinear problems. It is an approximation since $s^2=S/(N-p)$ was assumed to be equal to σ^2 (or the variance) and also the sensitivity coefficients are functions of the estimated parameters.

Chapter 4

Experimental Procedure

4.1 Epoxy Preparation:

The first step of the experimental work was the preparation of the epoxy. The preparation was done in the MSU Composite Materials and Structures Center. The amine epoxy resin was prepared using EPON 828 resin (Shell Chemical Company) and 1,3 Phenylenediamine (MPDA, $C_6H_4(NH_2)_2$) from the Aldrich Chemical Company as the curing agent.

The curing agent (mPDA) is a suspected carcinogen. In order to avoid health hazards, extreme caution was taken in handling this agent. First, rubber disposable gloves were worn at all times during the preparation of the epoxy to avoid contact with the skin. Also, goggles were necessary to shield the eyes from any accidental contact with the curing agent. In addition, a respirator was used to protect the respiratory system from any inhalation of the agent, and a lab coat was worn during the preparation in order to protect personal clothing from being stained. After the epoxy was prepared, all the laboratory apparatus used in the preparation was thoroughly cleaned.

A detailed explanation of the epoxy preparation procedure is presented below:

1. After wearing the protective clothes mentioned earlier, the EPON 828 resin and the curing agent (MPDA) were taken out of cold storage.
2. Two disposable plastic beakers and a spatula were cleaned with acetone and wiped dry. Foil was spread in a fume hood to avoid the spilling of the crystalline of the

MPDA.

3. An appropriate amount of resin was poured in one of the beakers and placed in an oven preheated to approximately 70°C. The amount of the resin needed was calculated using the one to one equivalency (i.e., 0.0855 kg of resin is needed with 0.0145 kg of MPDA, Rich, 1987).

4. Then, the second beaker was tarred. An approximate amount of MPDA was scooped into the tarred beaker using the cleaned spatula, and the weight indicated by the scale was recorded.

5. The second beaker with MPDA was placed in the oven with the resin. The MPDA was stirred occasionally for uniform melting.

6. After the MPDA was completely melted, the two beakers were removed from the oven, and the beaker with the MPDA was tarred on the scale. Then, the amount of resin calculated earlier was poured into it while stirring. Once done, the beaker with the mixed epoxy was placed in a 60°C preheated vacuum oven (VWR Scientific, Inc. Model 1410) and the pressure was reduced to -99 kPas. The vacuum was applied until the bubbles within the resin had diminished.

7. The beaker was then taken out of the oven, and sterile syringes were filled with the epoxy and placed in cold storage for future use.

8. The fume hood was cleaned and the spatula was washed with acetone.

Once the epoxy was prepared, it was kept in a cold storage place to limit the occurrence of curing reactions; a new batch was prepared every few days.

4.2 The Perkin-Elmer Differential Scanning Calorimeter (DSC):

A Perkin-Elmer DSC was used to cure the epoxy resin. The heat generated during

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during curing was monitored using the DSC system; this data was used to analyze the kinetics of the degree of cure of epoxy. The following section is devoted to a description of the Perkin-Elmer DSC and an explanation of its operating procedures.

4.2.1 General Description of the Perkin-Elmer DSC or DSC 7:

The DSC 7 is a computer-controlled instrument that functions using the power compensation design. With the use of a personal computer (PC), the DSC 7 regulates the collection of calorimeter measurement and the characterization and analysis of thermal properties of materials. The DSC 7 monitors the temperature of a sample throughout an experiment. In fact, it can be programmed over a designated time interval using a constant or a ramped temperature scan. The temperature can range from ambient temperature (25°C) up to 730°C, and with a coolant circulating accessory, the DSC 7 can operate at a sub-ambient temperature (as low as -170°C). Platinum resistance heaters and thermometers are used to precisely measure the energy and the temperature of the sample and the reference holder (temperature accuracy ±0.1°C). A continuous, automatic and precise control of the heaters is necessary to keep the temperature of the sample identical to the reference temperature.

The Perkin-Elmer DSC consists of four important components in addition to the PC, which is not provided by Perkin-Elmer Corporation (Figure 4.1). The four components are the DSC 7 Differential Scanning Calorimeter, the TAC7/pc Thermal Analysis Controller, the GSA 7 Gas Selector Accessory, and the high resolution Graphics Plotter. The DSC 7 Differential Scanning Calorimeter (Figure 4.3) is a computer controlled instrument which operates with a power composition design. It permits fast and direct calorimetric measurements and analysis of thermal properties of materials with i

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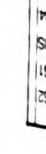
high accuracy. The TAC 7/PC is the intelligent high speed microprocessor that links the PC to the thermal analysis module and controls all its functions. The GSA 7 is a computer controlled device which permits automatic switching of purge gases at operator selected intervals. The fourth part is a high resolution graphics plotter which is controlled directly from the a computer menu. It generates multiple color plots with an automatic scaling performed by the PC. The specifications for each of these four parts are in Appendix A.

4.2.2 Sample Preparation for DSC:

The first step of the DSC analysis of an epoxide resin cure is to encapsulate an amount of the epoxy for use in the DSC. Several types of sample pans and covers (e.g. aluminum, gold, copper and platinum) can be used with the DSC 7, and the choice depends upon the nature of the sample and temperature range of operation. For instance, a gold pan cannot be used with a lead sample since lead alloys with gold, and an aluminum pan should never be used with temperature exceeding 600°C, since aluminum melts at 660°C. The standard aluminum sample pans and covers were used for the analysis of the curing of the EPON 828 resin with MPDA, since the temperature range of operation is between 70°C and 130°C.

A detailed description of the preparation procedure for a DSC sample is presented below:

1. After wearing the protection clothes, one of the syringes containing the epoxy was taken out of the cold storage.
2. The weight of an aluminum pan cover was recorded. An aluminum pan was placed on the scale, weighed and then tarred.
3. The aluminum pan was removed from the top of the scale, an amount of epoxy



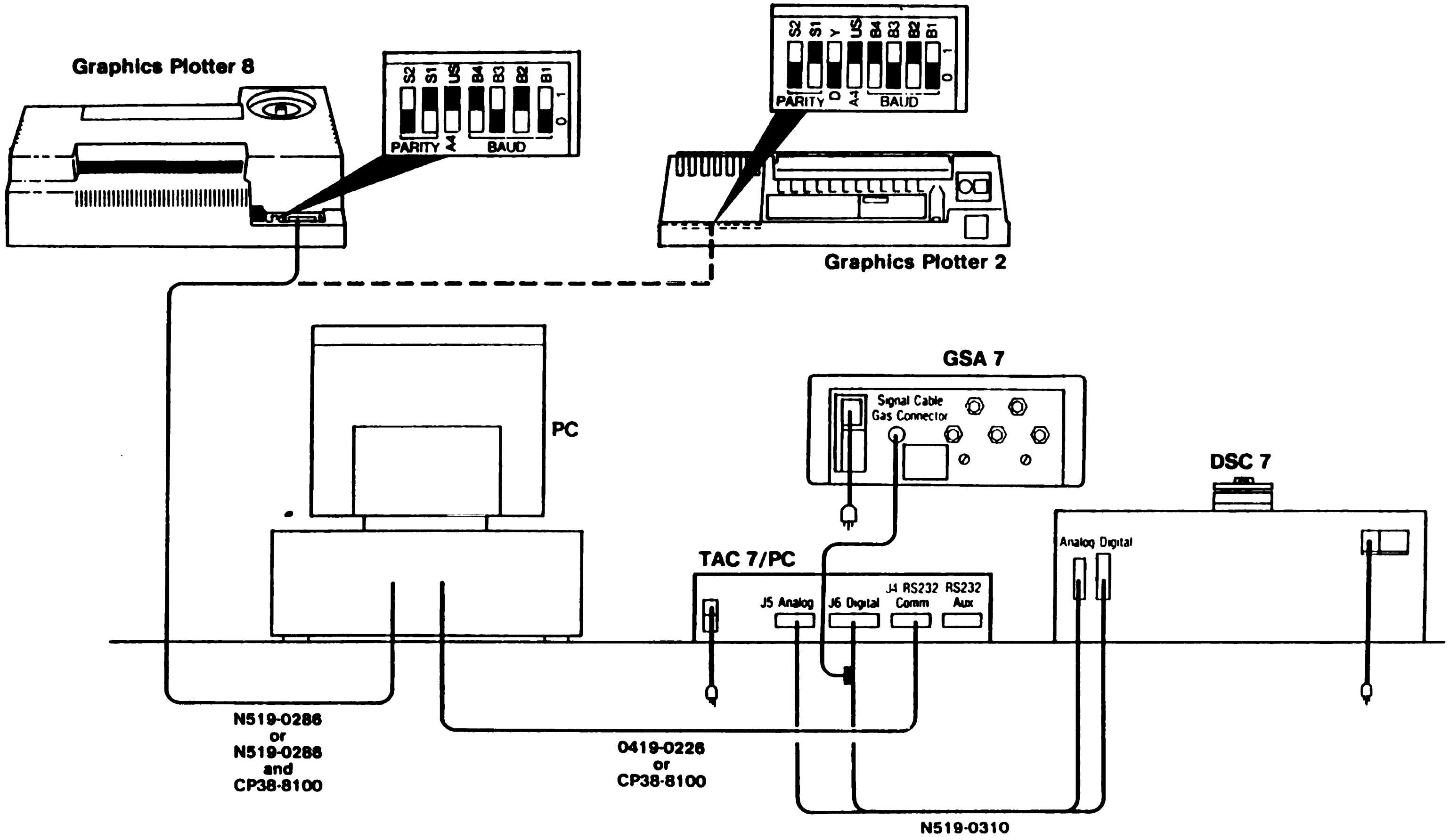


Figure 4.1 Schématic of the Perkin-Elmer Differential Scanning Calorimeter (from The DSC 7 Operator's Manual. Permission Granted by Perkin-Elmer Corporation to Use this Figure)

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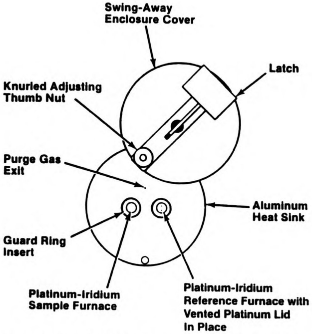

Figure 4.2 Schematic of the DSC 7 Sample Holder (Permission to Use this Figure Was Granted by the Perkin-Elmer Corporation)

Figure 4.3 Photograph of the Perkin-Elmer DSC7

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(between 5 and 15 mg) was placed in it, and then the pan was re-weighed.

4. The cover was placed carefully on the sample pan. Then, the sample pan was placed in a crimper's recess, and the crimper's handle was pressed down.

Once the DSC sample was prepared, it was used immediately in the DSC curing analysis. In case a DSC experiment was delayed, the sample was stored in a cold place.

4.2.3 Isothermal DSC Curing Procedure:

This section provides a detailed explanation for setting up and performing experiments on the Perkin-Elmer DSC. A typical DSC procedure includes three major steps. First, an epoxy sample is monitored during curing, and the experiment is repeated under identical conditions to create a baseline data file. The final step includes the analysis of the data obtained in each of these experiments.

The DSC 7 is supported with an advanced menu driven software facility which enables the user to control the experiment. A detailed explanation of the experimental procedure using the DSC is presented below.

1. After the DSC sample preparation, all the parts of the DSC setup (DSC 7, TAC 7/PC, Graphics Plotter, GSA 7 and the PC) were switched on. If they were already turned on, the TAC 7/PC was turned off for a few seconds and turned back on.

2. Once the READY indicator on the DSC 7 was displayed, the software menu was initiated by typing TA. Then, the menu would display two options: experiment setup and data analysis. For the first stage of the experiment, the setup option was selected.

3. The PARAMETERS option in the setup menu was selected to set the experimental parameters. A sample set of parameters for a typical isothermal run at 120°C is presented in Table 4.1.

Table 4.1 Sample Set of Experimental Parameters for Isothermal DSC Experiment.

Parameters	
Final Temperature:	120.0°C
Starting Temperature:	120.0°C
Scanning Rate:	0.0°C/min
Final Time:	60.00 min
Sample Weight:	7.7 mg
Multitasking:	No

4. The conditions option was then used to set or modify the run conditions which describe the status of the analyzer during and after the run. A sample set of conditions for a 120°C DSC run is presented in Table 4.2.

5. The direct control option was selected to drive the sample and the reference furnace to the desired cure temperature. Subsequently, the CONTROL and HEATING indicators at the front panel of the DSC 7 lit up. Once the desired temperature was reached, the HEATING indicator turned off.

6. The crimped sample was quickly placed in the platinum-iridium sample furnace and covered by the swing-away enclosure cover. Then, the latch was pressed fully down to tighten the seal.

7. The BEGIN RUN option was immediately selected.

Table 4.2 Sample Set of Run Conditions for an Isothermal DSC Experiment

Set Conditions:	
End Condition:	Stop
Load Temperature:	120.0°C
Ramp Rate to Load Temperature:	200.0°C/min
Data Delay :	0.0 min.
Event 1 Time:	0.00
Event 2 Time:	0.00
Initial Heat Flow:	20.0 mW

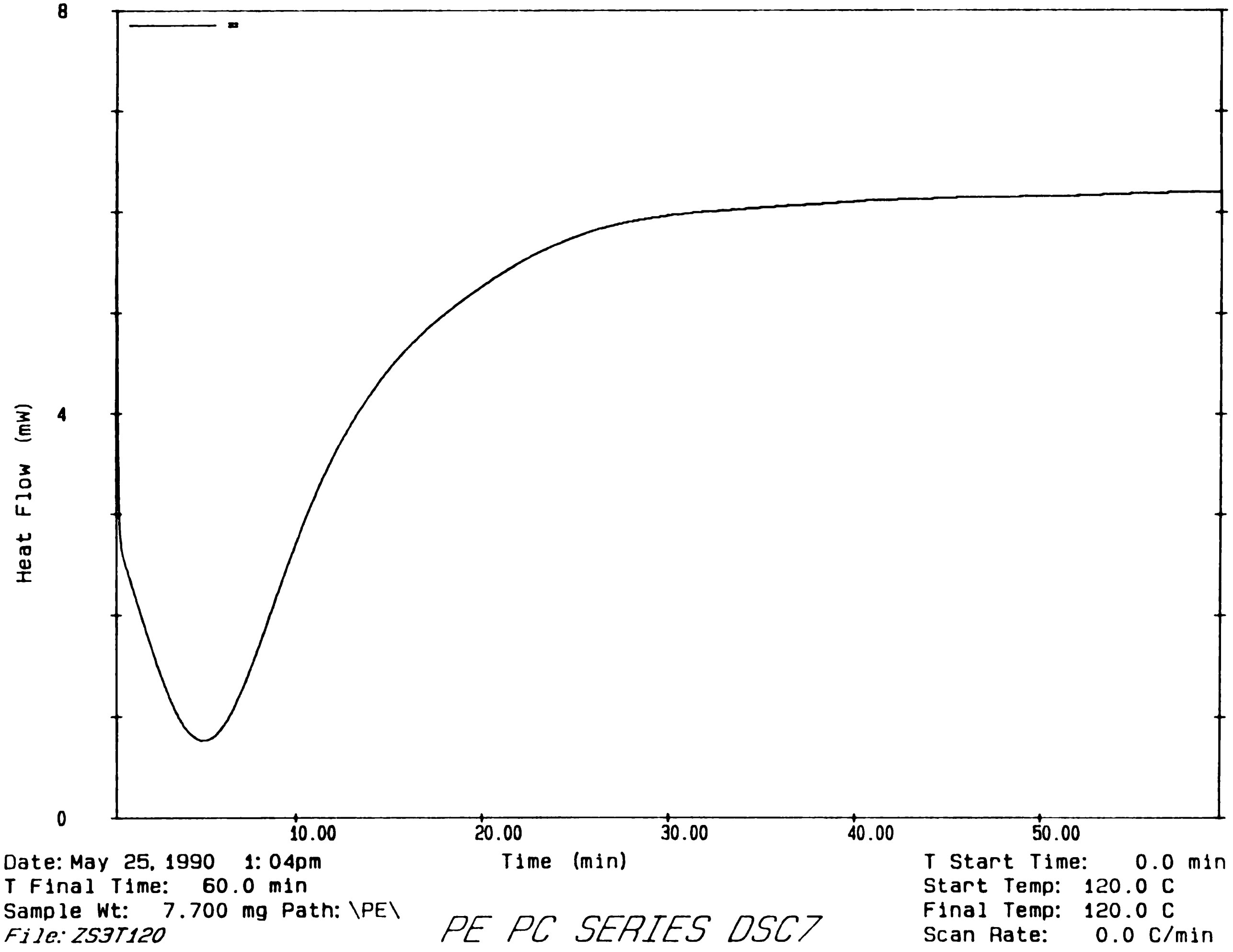


Figure 4.4 Perkin-Elmer DSC Output for an Isothermal Epoxy Cure

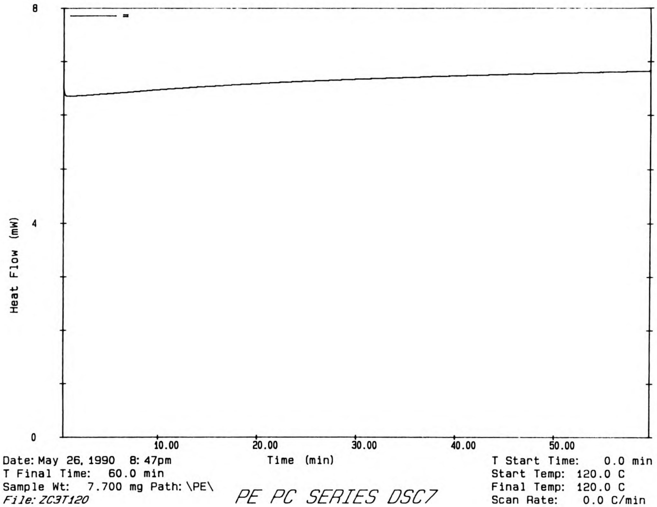


Figure 4.5 DSC Output for an Isothermal Baseline Experiment

8. Once the experiment is finished, the data (Figure 4.4) was stored by selecting the SAVE DATA option.

The same procedure was followed for the baseline run. In addition, the same parameters, conditions, and sample (now cured) that were used in the cure run were used in this run. The data collected was stored in a different file for future data analysis (Figure 4.5).

In the third step of the experiment, the DATA ANALYSIS option was selected. The two data files created earlier were recalled at the same time, and the heat flow data of the curing run was subtracted from the data of the baseline experiment in order to obtain the net heat flow from the epoxy sample during cure (Figure 4.6).

The curing process of the epoxy was analyzed using experimental data from isothermal experiments at four different temperatures as shown in the Table 4.3. A typical cure cycle for EPON 828-amine carbon composite consists of an isothermal cure at 75°C followed by an isothermal cure at 125°C. Based on these curing temperatures, the following isothermal cure temperatures were selected for the isothermal experiments: 70°C, 80°C, 120°C, and 130°C.

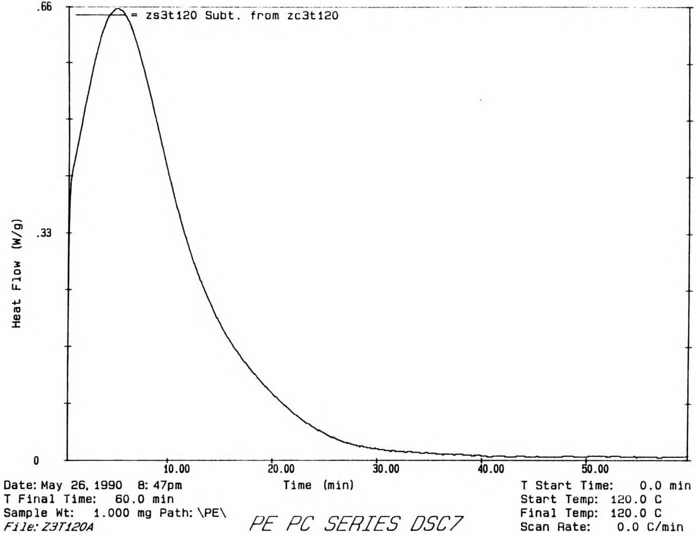


Figure 4.6 The Perkin-Elmer Isothermal Curing Output After Subtracting the Baseline Data.

Table 4.3 Experimental parameters for isothermal epoxy curing experiments.

Temperature (°C)	Run Number	Time (min.)	Sample Weight (mg)
70	1	360	7.9
	2	360	8.8
	3	360	8.3
80	4	140	7.7
	5	140	10.2
	6	140	10.3
120	7	60	7.7
	8	60	9.3
	9	60	6.2
130	10	45	5.6
	11	45	8.6
	12	45	7.4

4.2.4 Dynamic DSC Curing Procedure:

The dynamic DSC procedure implies that the temperature of the epoxy varies linearly with respect to time throughout the curing process. The purpose of the dynamic cure experiment is to determine the total amount of heat released by unit mass of epoxy during a 100% cure. The same DSC procedure used in the isothermal experiments was performed with only few modifications. The scanning rate was changed from 0.0 °C/min for the isothermal runs to 4.0 °C/min, and the initial and final temperature values were 25°C and 200°C, respectively. The final temperature was chosen to ensure completion of the kinetic reactions.

The area under the curve (heat released by unit of mass sample) was computed for each of the three experiments (Figure 4.7). The average of the three values of the heat flow was used to determine the degree of cure from the isothermal data. Table 4.4 summarizes the experimental parameters for all three dynamic DSC experiments.

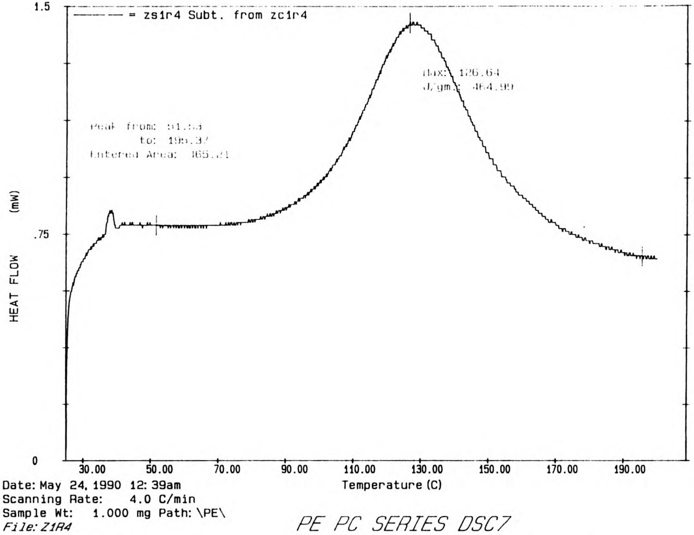


Figure 4.7 Perkin-Elmer DSC Dynamic Epoxy Curing Output

Table 4.2 Experimental parameters for epoxy curing using dynamic DSC experiments.

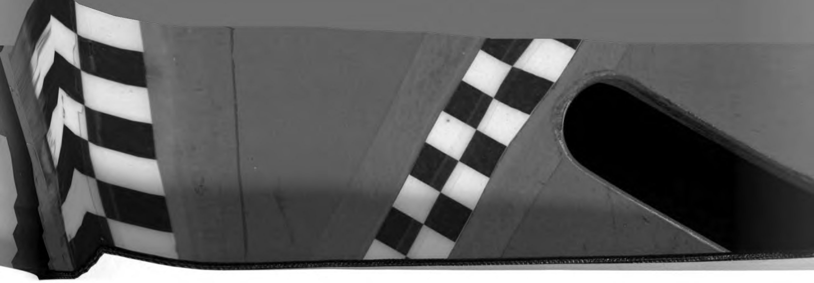
Exp. number	Initial Temp.	Final Temp.	Sample Weight	Generated Heat
1	25 °C	200 °C	7.3 mg	464.99 J/g
2	25 °C	200 °C	10.0 mg	453.8 J/g
3	25 °C	200 °C	9.6 mg	449.0 J/g

4.3 Eumetric System III Microdielectrometer:

4.3.1 General Description of the Eumetric System III Microdielectrometer:

The Eumetric System III is an integrated dielectric setup which analyzes, regulates and optimizes the properties and the preparation of composites, polymers and other kinds of materials. This system excites materials with dielectric sensors by applying a time varying voltage, and then measures their dielectric properties. This dielectric system can be monitored either manually with its front panel or remotely with standard eumetric software and data analysis options.

The dielectric setup consists of four principle components and associated software. The components are the system III Microdielectrometer, the Eight Channel Multiplexer, the Eumetric Programmable Oven, and the low conductivity integrated circuit Sensor. The System III Dielectrometer is an integrated dielectric measurement system which monitors and optimizes the dielectric properties of materials. It includes a microprocessor to control its frequency synthesizer, analog-to-digital converter, and 256K memory. The Eight Channel Multiplexer provides the internal software and the connectors required for eight sequential measurements. The Eumetric Programmable Oven (Figure 4.8) consists of a chassis and a sample chamber. The sample chamber is



mounted on the chassis and consists of a round stage with a horizontal sample surface (2.25" diameter). Heaters and cooling coils are located below the sample stage. The low conductivity integrated circuit measures dielectric properties and temperature with high accuracy. The sensor chip (Figure 4.9) consists of a sensing area, amplifying transistors, and a thermal diode. A detailed description of each of these elements is presented in Appendix B.

The measurement technique of the System III microdielectrometer is based on the generation of synthesized excitations with frequencies regulated by a crystal oscillator. The sensors pass these voltage excitations to the material sample, and in response a current is observed through the material. The System III samples this response along with the temperature of the sample, stores the data, and performs correlations with the excitation waveform to obtain the magnitude and the phase of the response.

4.3.2 Isothermal Dielectric Curing Process:

In this section, a detailed explanation of the curing process on the Eumetric System III Microdielectrometer is presented. Unlike the DSC experimental procedure, this procedure does not require the use of small samples in crimped aluminum pans.

The first step in the curing experiment is the setup of the oven at the desired temperature. The Eumetric programmable oven enables the user to control the temperature of the sample chamber as a linear function with respect to time or as a constant ranging from -150°C to 500°C. Since the sample chamber was initially at ambient temperature, the temperature was first ramped quickly from ambient to the desired isothermal curing temperature. Then, the oven was programmed to keep the sample chamber at the desired temperature for a time period longer than the

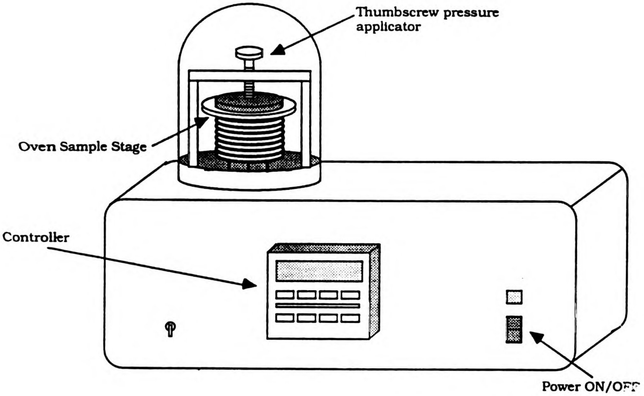


Figure 4.8 Schematic of the Eumetric Programmable Oven (Permission granted by Micromet Instruments to use this figure)

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Figure 4.8 Schematic of the Eumetric Programmable Oven (Permission granted by Micromet Instruments to use this figure)

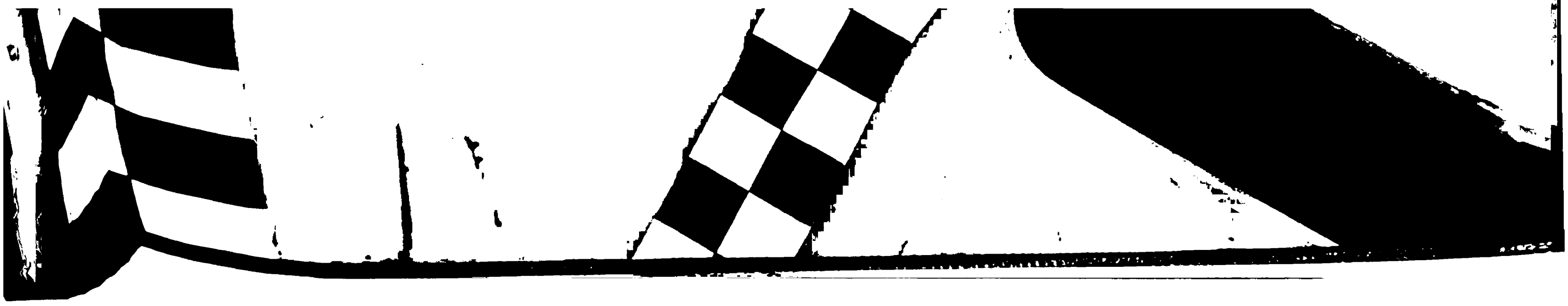

Figure 4.9 The Eumetric Low Conductivity Integrated Circuit Sensor (Permission granted by Micromet Instruments to use this figure).

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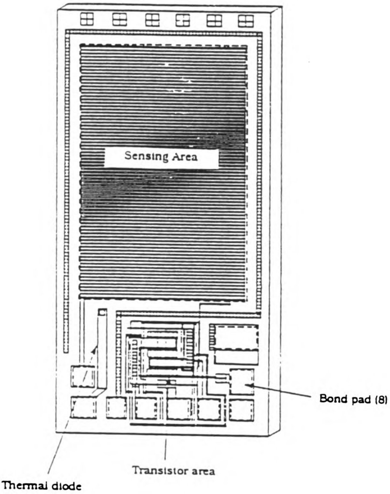

Figure 4.9 The Eumetric Low Conductivity Integrated Circuit Sensor (Permission granted by Micromet Instruments to use this figure).

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During the second phase of the setup, the experimental parameters were entered. These parameters include information on the multiplexer channel, low conductivity sensor, thermocouple channel, excitation frequencies, sensor ID and the duration of the data collection. Once all these parameters were entered, the computer program was ready to start scanning the temperature, dielectric loss factor and permitivity of the sample.

The final phase of the preparation was to take the epoxy out of the cold storage, place an appropriate amount (≈1g) on the sample surface in the oven chamber, set the sensing area of the low conductivity sensor against the epoxy and press it using the thumbscrew pressure applicator. Then, the oven stage was covered with the a glass cover for protection and isolation from heat loss. The data scanning was initiated directly after finishing the last phase of the setup.

Table 4.5 Experimental parameters for epoxy curing using Dielectric experiments.

Temperature (°C)	number of runs	duration (min)
70	3	180
80	3	90
120	3	60
130	3	45

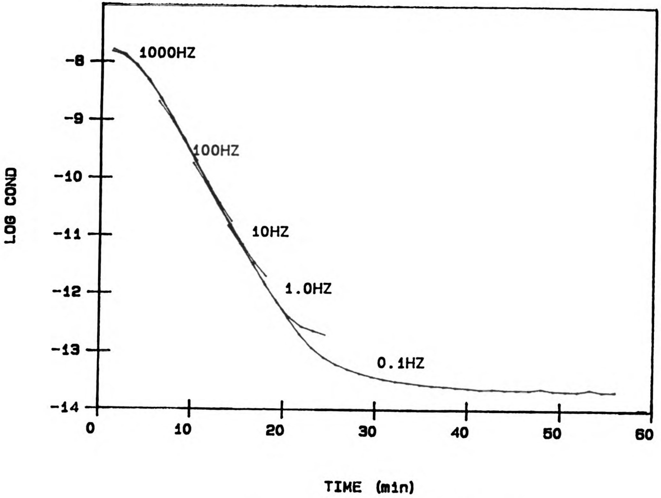
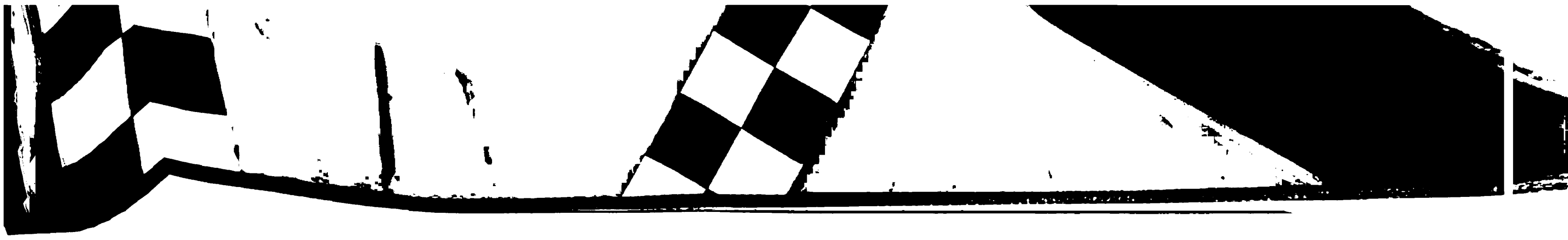


Figure 4.10 Isothermal Dielectric Curing Output.

4.3.3 Dynamic Dielectric Curing Process:

In order to determine the log conductivity associated with a 100% epoxy cure, a dynamic dielectric experiment was performed. The same procedure used in the isothermal experiment was followed for the dynamic case. The only modification, that was performed, is in the programming of the oven. In this case, the temperature of the oven was ramped from ambient temperature up to 200°C with a rate of 4°C/min. The reset of the experiment parameters was kept the same as in the isothermal case.



Chapter 5

5. Results and Discussion

In this chapter, the results, including the sensitivity coefficient analysis and the estimation of kinetic parameters using both the linear regression and the Box-Kanemasu estimation methods from DSC and dielectric data, will be presented and discussed. An analysis of the sensitivity coefficients is first presented, followed by the results of the parameter estimation procedures using DSC data. The results obtained from the dielectric data will then be presented. A comparison of the two experimental procedures and the two estimation methods for the three kinetic models investigated will be presented in the last section of this chapter.

5.1 Sensitivity Coefficient Analysis:

Investigation of the sensitivity coefficients can give insight into the appropriateness of the model and the estimation procedure. Linear dependence between the sensitivity coefficients of different parameters signifies that the parameters are correlated and cannot be estimated uniquely using the Box-Kanemasu method (Beck and Arnold, 1977). Even near linear dependence of the sensitivity coefficients can result in inaccurate estimates. Linear dependence can be easily investigated by plotting the sensitivity coefficients of different parameters against each other.

The sensitivity coefficients calculated assuming $d\alpha/dt$ measurements for the two rate constants in the first and second models (eqs. (3.1) and (3.2)) and the rate constant

and exponential in the third model (eq. (3.3)) were first analyzed. In all three cases, near linear dependence was found between the parameters. The sensitivity coefficients for the two rate constants in the first kinetic model are shown in Figure 5.1 and Figure 5.2 shows the relationship between the two parameters. Note that even though the parameters are not linearly dependent over the entire range investigated, the near linear dependency for early times would result in inaccurate parameter estimates.

The sensitivity coefficients were again calculated and compared assuming measurements of α in eq. (3.23). In this case, the sensitivity coefficients were found to be uncorrelated for all three kinetic models. The sensitivity coefficients for the first kinetic model ($K_1\partial\alpha/\partial k_1$ and $k_2\partial\alpha/\partial k_2$) are shown in Figure 5.3 and compared in Figure 5.4. Note that there is much less evidence of linear dependence in Figure 5.4 compared with Figure 5.2. In addition, the sensitivity coefficients calculated using α as the measured variable are three orders of magnitude larger than those determined using $d\alpha/dt$ as the measured quantity, this indicates that α is more sensitive to changes in the parameters being estimated, and therefore, it is more advantageous to have higher sensitivity coefficients in the estimation procedure. Therefore, due to the possibility of correlation among the parameters and due to the small magnitude of the sensitivity coefficients found using $d\alpha/dt$ as the measured variable, all parameter estimates were found assuming α as the measured quantity, so that the sensitivity coefficients were calculated using α for Y_p in eq. (3.23) rather than $d\alpha/dt$. This required that the DSC reduced data ($d\alpha/dt$) be numerically differentiated to obtain α prior to the estimation procedure.

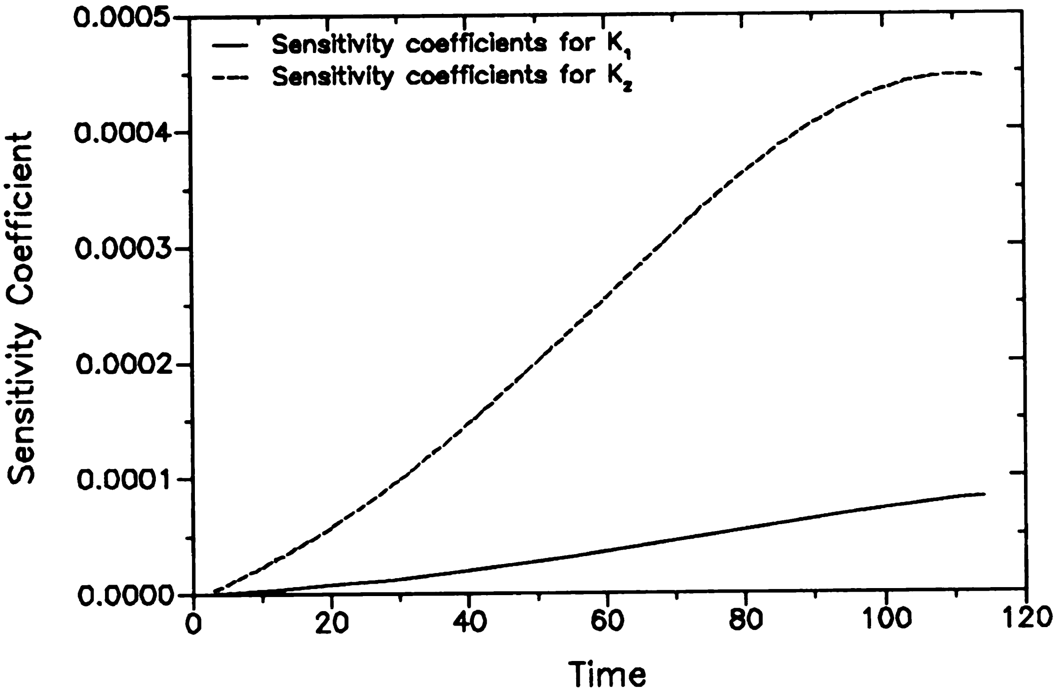


Figure 5.1 Sensitivity coefficients of K_1 and K_2 vs Time for Model 1 Using DSC Data.

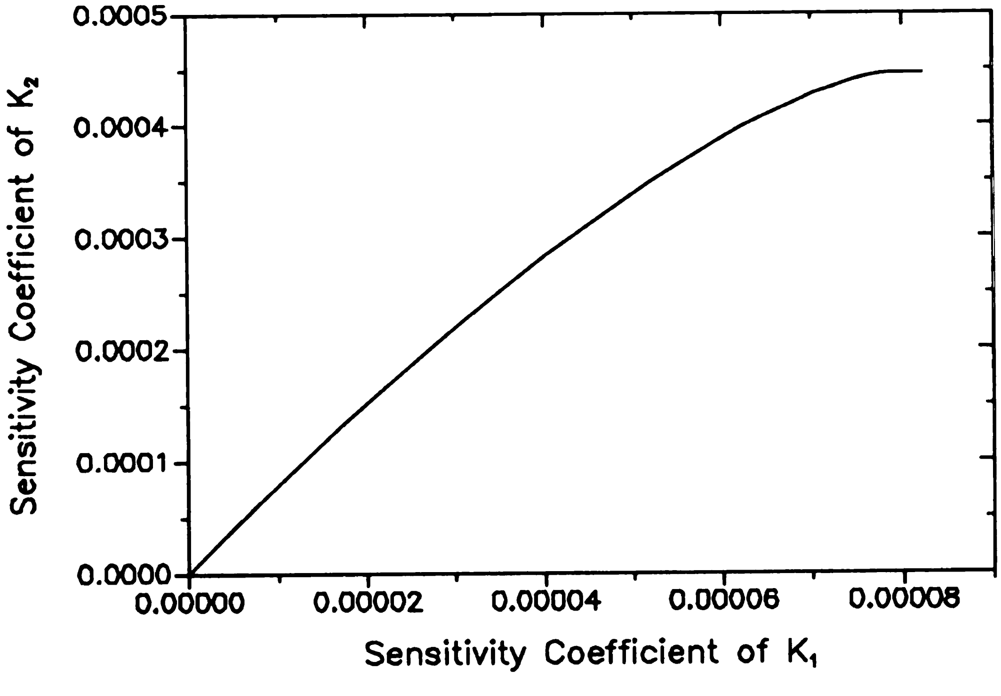


Figure 5.2 Sensitivity Coefficient of K_2 vs Sensitivity Coefficient of K_1 for Model 1 Using DSC Data.

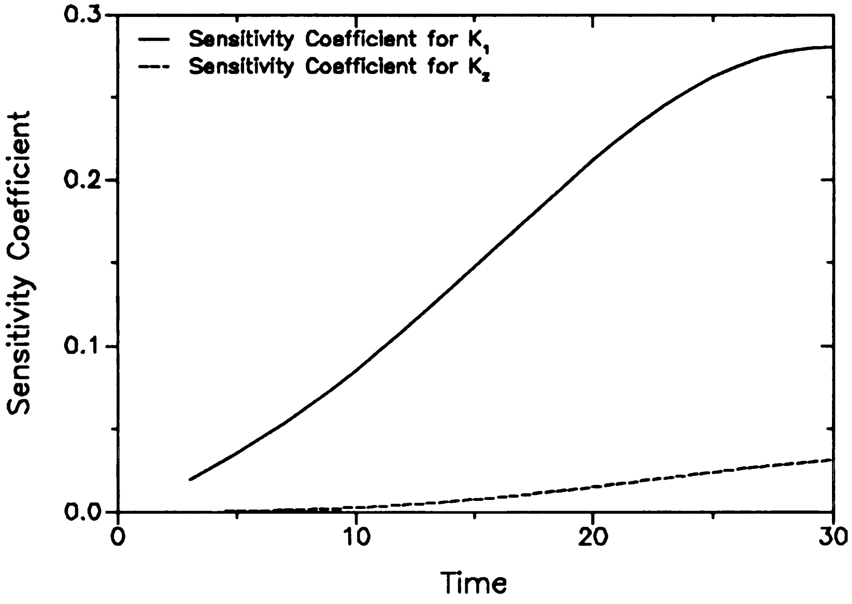


Figure 5.3 Sensitivity Coefficient of K_1 and K_2 vs Time For Model 1 Using Dielectric Data

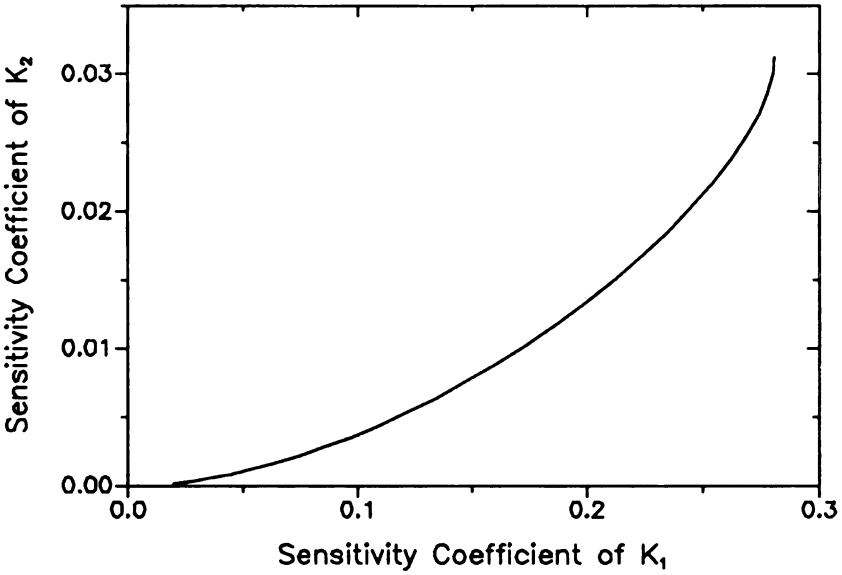


Figure 5.4 Sensitivity Coefficient of K_2 vs Sensitivity Cofficient of K_1 for Model 1 Using Dielectric Data.

5.2 Estimation of Cure Kinetic Parameters of EPON 828/mPDA Epoxy Using DSC Data:

The kinetic parameters for the three kinetic models presented in Chapter 3 (eq.(3.1), (3.2), and (3.3)) were first estimated using DSC data. The two methods of estimation, the linear regression and the Box-Kanemasu minimization methods, will be employed to determine the rate constants, and the Arrhenius constants associated with each of the three models presented in eqs. (3.1), (3.2) and (3.3). These models will be referred to as Model 1 (eq. (3.1)), Model 2 (eq. (3.2)), and Model 3 (eq. (3.3)) in subsequent discussions.

5.2.1 Estimation of the Kinetic Parameters from DSC data For Model 1:

5.1.1.1 Estimation Using Linear Regression:

The rate constants K_1 and K_2 for Model 1 were estimated for each isothermal DSC experiment shown in Table 4.1. The degree of cure rates were first calculated for each of these experiments from the heat of reaction data and the total heat of reaction obtained from the dynamic experiments. The degree of cure was then obtained by numerical integration. The rate constants were then estimated from eq.(3.16) for each isothermal experiment using the least squares method associated with PLOTit^R (1989) software. The left hand-side of eq. (3.13) for one experiment is shown plotted against α in Figure 5.5. The estimated curve is shown by the solid line with the 95% confidence bands. The estimated parameters (K_1 and K_2) along with 95% confidence intervals are displayed in Table 5.1 for each of the isothermal experiments.

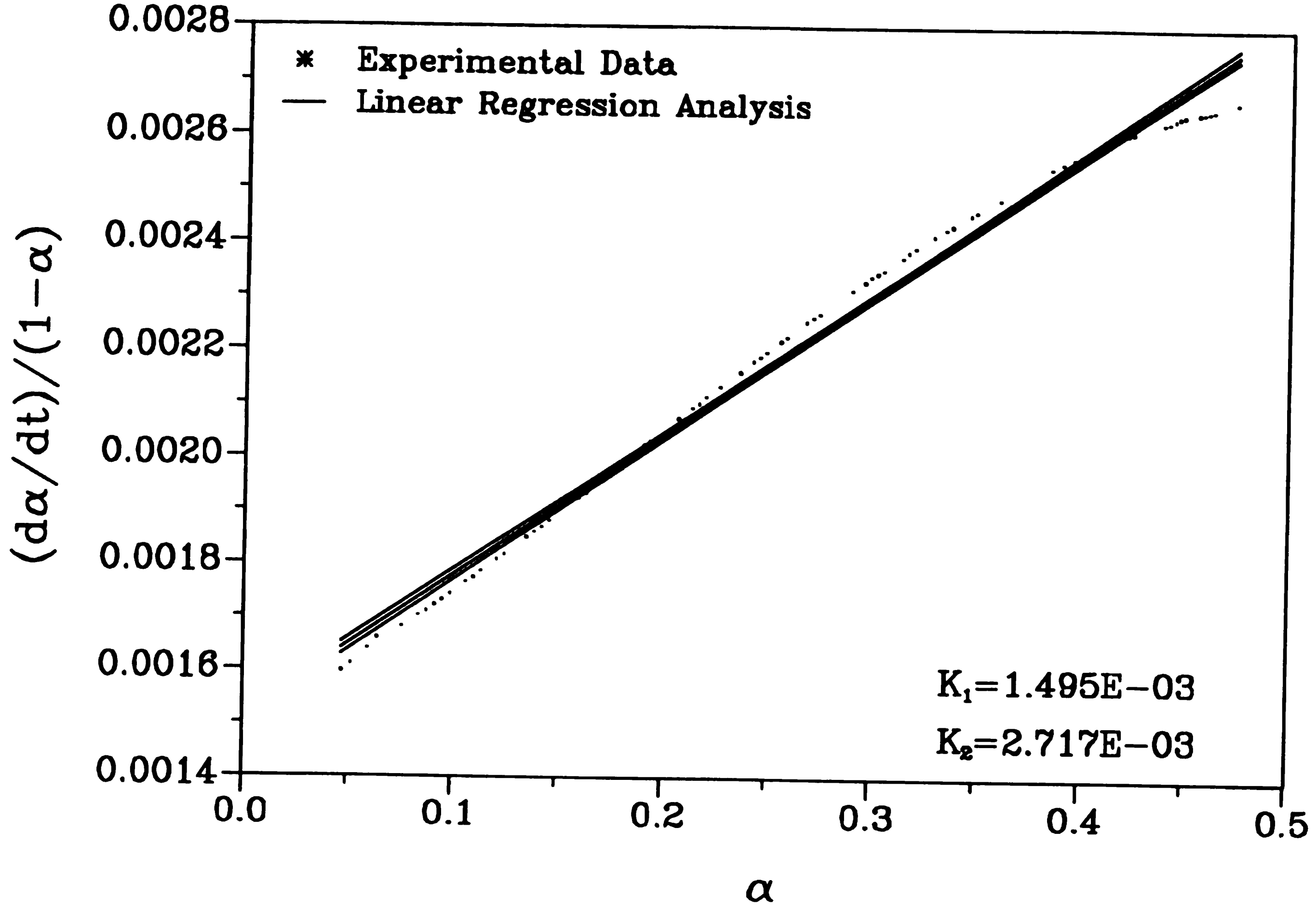


Figure 5.5 Estimation of the Rate Constants for Experiment 10 (Table 5.1) for Model 1 Using DSC Data.

Table 5.1 Estimated Rate Constants and Associated 95% Confidence Intervals for Model 1 Using the Linear Regression Method and DSC Data.

Exper. No.	Temp. (°C)	Least Squares Method	
		K_1 (s^{-1})	K_2 (s^{-1})
1	70	$(4.26\pm0.19)\times10^{-5}$	$(3.77\pm0.08)\times10^{-4}$
2	70	$(5.68\pm0.14)\times10^{-5}$	$(3.91\pm0.04)\times10^{-4}$
3	70	$(5.01\pm0.17)\times10^{-5}$	$(3.85\pm0.07)\times10^{-4}$
4	80	$(7.46\pm0.08)\times10^{-4}$	$(6.19\pm0.04)\times10^{-4}$
5	80	$(4.81\pm0.15)\times10^{-4}$	$(7.05\pm0.06)\times10^{-4}$
6	80	$(1.42\pm0.01)\times10^{-4}$	$(6.55\pm0.02)\times10^{-4}$
7	120	$(6.36\pm0.05)\times10^{-4}$	$(3.76\pm0.01)\times10^{-3}$
8	120	$(8.15\pm0.05)\times10^{-4}$	$(3.69\pm0.01)\times10^{-3}$
9	120	$(1.41\pm0.02)\times10^{-3}$	$(3.58\pm0.07)\times10^{-3}$
10	130	$(1.49\pm0.01)\times10^{-3}$	$(2.72\pm0.04)\times10^{-3}$
11	130	$(1.55\pm0.01)\times10^{-3}$	$(3.24\pm0.03)\times10^{-3}$
12	130	$(6.17\pm0.07)\times10^{-4}$	$(5.87\pm0.01)\times10^{-3}$

The results obtained from the estimation of the rate constants were used for estimation of the activation energy constants (E_i) and the pre-exponential constants (A_i) using the procedure discussed in Section 3.3.1 and PLOTit^R (1989) software. The estimated linear regression curves including 95% confidence bands for one experiment are shown in Figure 5.6 for K_1 and in Figure 5.7 for K_2. The resulting estimated parameters from these figures ($\ln(A_1)$, E_1, $\ln(A_2)$, and E_2) along with the computed 95% confidence intervals are shown in Table 5.2.

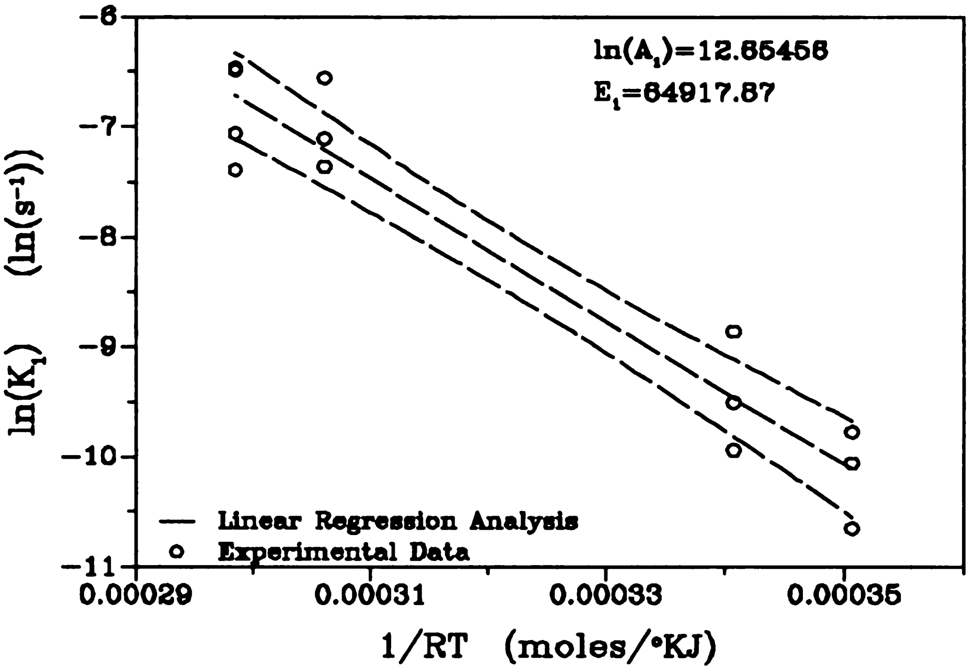


Figure 5.6 Estimation of ln(A_1) and E_1 for Model 1 Using DSC Data.

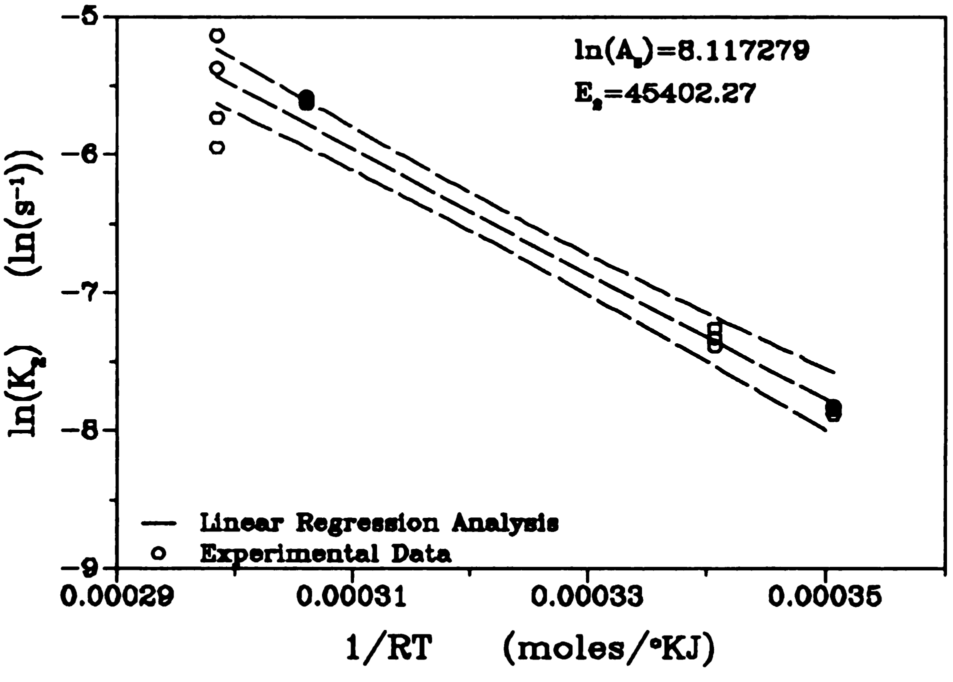


Figure 5.7 Estimation of ln(A_2) and E_2 for Model 1 Using DSC Data.

Table 5.2 Estimated Activation Energy and Pre-exponential Constants and Associated 95% Confidence Intervals for Model 1 Using the Linear Regression Method and DSC Data:

$\ln(A_1)(\ln(s^{-1}))$	E_1 (kJ/mole)	$\ln(A_2)$ $(\ln(s^{-1}))$	E_2 (kJ/mole)
12.93±1.57	68.19±2.81	10.70±1.47	51.0867±3.9836

5.2.1.2 Estimation of the Kinetic Parameters Using the Box-Kanemasu Method:

The Box-Kanemasu then was used to estimate the rate constants for Model 1 using the DSC experiments. This method was implemented using Fortran program NLINA (Appendix C). In this program, two subroutines were modified for this application. One subroutine is the model subroutine in which the calculated values of α are determined from the solution of the differential equation (eq. 3.1). The sensitivity coefficients are calculated in the second subroutine. Both of these subroutines are shown in Appendix C. These subroutines were modified twice; first for the estimation of the rate constants and then for the estimation of the pre-exponential constants and the activation energy constants. Prior to the estimation procedure, the DSC data was arranged in a data file as shown in Appendix C. The Arrhenius constants were estimated directly by using the data from all of the isothermal experiments, in this case, a data file was created by stacking all of the isothermal files together.

The estimates and 95% confidence intervals for the individual rate constants using the Box-Kanemasu estimation method are shown in Table 5.3, and the estimates and 95% confidence intervals for the Arrhenius constants in Table 5.4. The confidence regions were determined using the method presented in Section 3 (eq.(3.28)). The values of P_{ii} and S were obtained from the computer program NLINA.

Table 5.3 Estimated Rate Constants and Associated 95% Confidence Intervals for Model 1 Using the Box-Kanemasu Method and DSC Data.

Exper. No.	Temp. (°C)	Box-Kanemasu Method	
		K_1 (s^{-1})	K_2 (s^{-1})
1	70	$(4.20\pm0.09)\times10^{-5}$	$(5.41\pm0.10)\times10^{-4}$
2	70	$(4.71\pm0.11)\times10^{-5}$	$(4.03\pm0.10)\times10^{-4}$
3	70	$(4.31\pm0.08)\times10^{-5}$	$(4.63\pm0.05)\times10^{-4}$
4	80	$(1.81\pm0.01)\times10^{-4}$	$(5.92\pm0.08)\times10^{-4}$
5	80	$(6.53\pm0.01)\times10^{-5}$	$(7.61\pm0.09)\times10^{-4}$
6	80	$(1.04\pm0.01)\times10^{-4}$	$(5.63\pm0.07)\times10^{-4}$
7	120	$(8.28\pm0.03)\times10^{-4}$	$(3.62\pm0.02)\times10^{-3}$
8	120	$(1.01\pm0.01)\times10^{-3}$	$(3.46\pm0.02)\times10^{-3}$
9	120	$(1.57\pm0.01)\times10^{-3}$	$(3.44\pm0.01)\times10^{-3}$
10	130	$(1.62\pm0.01)\times10^{-3}$	$(2.25\pm0.04)\times10^{-3}$
11	130	$(1.63\pm0.01)\times10^{-3}$	$(3.12\pm0.04)\times10^{-3}$
12	130	$(9.23\pm0.04)\times10^{-4}$	$(5.72\pm0.03)\times10^{-3}$

Table 5.4 Estimated Activation Energy and Pre-exponential Constants and Associated 95% Confidence Intervals for Model 1 Using the Box-Kanemasu Method and DSC Data.

$\ln(A_1)(\ln(s^{-1}))$	E_1 (kJ/mole)	$\ln(A^2)$ ($\ln(s^{-1})$)	E_2 (kJ/mole)
14.26±0.53	68.36±1.60	5.45±0.38	38.69±1.21

5.2.2 Estimation of the Kinetic Parameters from DSC data For Model 2:

The rate constants and Arrhenius constants associated with Model 2 were estimated using both the linear regression and Box-Kanemasu minimization methods.

5.2.2.1 Estimation Using Linear Regression:

The rate constants presented in eq. (3.2) were estimated for each of the isothermal experiments shown in Table 4.1 using PLOTit^R (1989) software as described in the analysis of Model 1. The results are shown in Table 5.5.

Table 5.5 Estimated Rate Constants and Associated 95% Confidence Intervals for Model 2 Using the Linear Regression Method and DSC Data.

Exper. No.	Temp. (°C)	Linear Regression Method	
		K_1 (s^{-1})	K_2 (s^{-1})
1	70	$(2.25 \pm 0.12) \times 10^{-5}$	$(6.94 \pm 0.05) \times 10^{-4}$
2	70	$(2.38 \pm 0.22) \times 10^{-5}$	$(7.82 \pm 0.09) \times 10^{-4}$
3	70	$(2.33 \pm 0.18) \times 10^{-5}$	$(7.41 \pm .06) \times 10^{-4}$
4	80	$(5.53 \pm 0.10) \times 10^{-5}$	$(1.54 \pm 0.03) \times 10^{-4}$
5	80	$(1.00 \pm 0.16) \times 10^{-5}$	$(1.23 \pm 0.07) \times 10^{-4}$
6	80	$(4.53 \pm 0.30) \times 10^{-5}$	$(1.09 \pm 0.01) \times 10^{-4}$
7	120	$(2.17 \pm 0.52) \times 10^{-4}$	$(7.88 \pm 0.20) \times 10^{-3}$
8	120	$(3.67 \pm 0.62) \times 10^{-4}$	$(3.46 \pm 0.02) \times 10^{-3}$
9	120	$(7.91 \pm 0.11) \times 10^{-4}$	$(9.66 \pm 0.38) \times 10^{-3}$
10	130	$(6.63 \pm 0.78) \times 10^{-4}$	$(1.07 \pm 0.02) \times 10^{-2}$
11	130	$(1.11 \pm 0.04) \times 10^{-3}$	$(7.68 \pm 0.14) \times 10^{-3}$
12	130	$(3.31 \pm 0.60) \times 10^{-4}$	$(1.01 \pm 0.03) \times 10^{-3}$

The same procedure used for Model 1 was also pursued to determine the activation energy constants and the pre-exponential factors. The results for the estimation of these parameters are presented in Table 5.6.

Table 5.6 Estimated Activation Energy and Pre-exponential Constants and Associated 95% Confidence Intervals for Model 2 Using the Linear Regression Method and DSC Data.

$\ln(A_1)(\ln(s^{-1}))$	E_1 (kJ/mole)	$\ln(A^2)$ $(\ln(s^{-1}))$	E_2 (kJ/mole)
14.26±0.53	68.36±3.80	5.45±0.38	38.69±1.21

5.2.2.2 Estimation of the Kinetic Parameters Using the Box-Kanemasu Method:

The same Box-Kanemasu procedure used for the estimation of the rate constants in Model 1, was also utilized for the estimation of the rate constants and the Arrhenius constants associated with Model 2. The results for the estimation of the individual rate constants are found in Table 5.7, while the estimated Arrhenius constants associated with K_1 and K_2 and 95% confidence intervals are shown in Table 5.8.

Table 5.7 Estimated Rate Constants and Associated 95% Confidence Intervals for Model 2 Using the Box-Kanemasu Method and DSC Data.

Exper. No.	Temp. (°C)	Box-Kanemasu Method	
		K_1 (s^{-1})	K_2 (s^{-1})
1	70	$(3.51\pm0.74)\times10^{-5}$	$(8.43\pm0.04)\times10^{-4}$
2	70	$(4.55\pm0.39)\times10^{-5}$	$(5.95\pm.051)\times10^{-4}$
3	70	$(4.13\pm0.61)\times10^{-5}$	$(7.03\pm.05)\times10^{-4}$
4	80	$(1.26\pm0.05)\times10^{-4}$	$(1.38\pm0.02)\times10^{-3}$
5	80	$(6.12\pm0.28)\times10^{-5}$	$(1.10\pm0.01)\times10^{-3}$
6	80	$(9.13\pm0.34)\times10^{-5}$	$(9.58\pm0.13)\times10^{-4}$
7	120	$(5.20\pm0.33)\times10^{-4}$	$(7.99\pm0.12)\ 10^{-3}$
8	120	$(6.55\pm0.41)\times10^{-4}$	$(8.28\pm0.15)\ 10^{-3}$
9	120	$(1.01\pm0.09)\times10^{-3}$	$(1.00\pm0.03)\ 10^{-3}$
10	130	$(1.32\pm0.03)\times10^{-3}$	$(8.44\pm0.10)\times10^{-3}$
11	130	$(1.41\pm0.03)\times10^{-3}$	$(6.53\pm0.09)\times10^{-3}$
12	130	$(4.74\pm0.42)\times10^{-4}$	$(1.19\pm0.018)\times10^{-2}$

Table 5.8 Estimated Activation Energy and the Pre-exponential Constants and Associated 95% Confidence Intervals for Model 2 Using the Box-Kanemasu Method and DSC Data.

$\ln(A_1)(\ln(s^{-1}))$	E_1 (kJ/mole)	$\ln(A^2)$ $(\ln(s^{-1}))$	E_2 (kJ/mole)
12.88±2.04	67.20±6.17	12.09±0.32	55.05±3.96

5.2.3 Estimation of the Kinetic Parameters from DSC Data for Model 3:

In this part, the results are presented for the estimation of the kinetic parameters associated with Model 3 (eq. (3.3)) from DSC data using the two methods of estimation employed with the other two models. The parameters that needed to be estimated were the rate constant and the exponential constant and the activation energy constant and the pre-exponential factor associated with the rate constant. The rate constant and the exponential n were first estimated using the linear regression with PLOTit^R software; the estimated curves and 95% confidence bands for one experiment are shown in Figure 5.8. The estimated parameters and 95% confidence intervals for the isothermal experiments are shown in Table 5.9, and the Arrhenius constants and 95% confidence intervals are shown in Table 5.10.

The kinetic parameters were then estimated using the Box-Kanemasu method; the results for the rate constant and the exponential n from each of the isothermal experiments are shown in Table 5.9. The Arrhenius constants were estimated from all of the isothermal data combined as discussed previously; results are shown in Table 5.10.

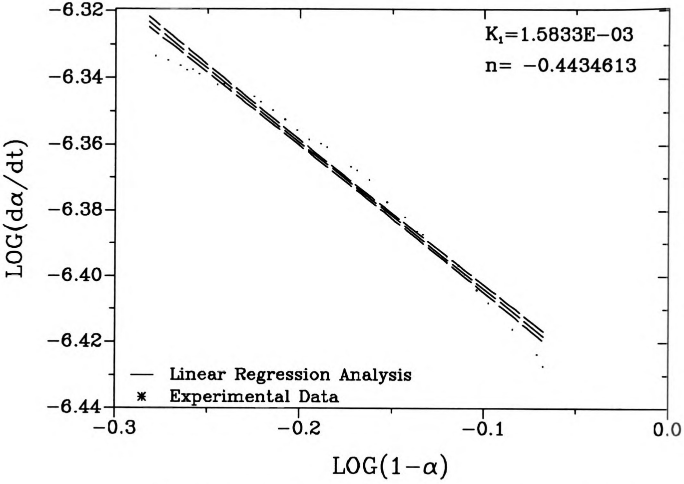


Figure 5.8 Estimation of K_1 and n for Exp. 10 for Model 3 Using DSC Data.

Table 5.11 Estimated Rate and Exponential Constants and Associated 95% Confidence Intervals for Model 3 Using the Box-Kanemasu Method and DSC Data.

Exper. No.	Temp. (°C)	Least Square Method	
		K_1 (s^{-1})	Exponential Constant
1	70	$(9.12\pm0.15)\times10^{-5}$	$(-1.26\pm0.22)\times10^{-2}$
2	70	$(8.43\pm0.10)\times10^{-5}$	$(-1.13\pm0.24)\times10^{-1}$
3	70	$(8.95\pm0.14)\times10^{-5}$	$(-1.72\pm0.36)\times10^{-2}$
4	80	$(2.24\pm0.01)\times10^{-4}$	$(-9.72\pm0.57)\times10^{-2}$
5	80	$(1.31\pm0.01)\times10^{-4}$	$(-9.94\pm2.05)\times10^{-3}$
6	80	$(1.53\pm0.01)\times10^{-4}$	$(-9.97\pm1.22)\times10^{-3}$
7	120	$(1.14\pm0.01)\times10^{-3}$	$(-1.01\pm0.10)\times10^{-2}$
8	120	$(1.28\pm0.01)\times10^{-3}$	$(-3.01\pm0.21)\times10^{-2}$
9	120	$(1.75\pm0.03)\times10^{-3}$	$(-5.03\pm0.11)\times10^{-2}$
10	130	$(1.76\pm0.02)\times10^{-3}$	$(-2.01\pm0.07)\times10^{-2}$
11	130	$(1.70\pm0.05)\times10^{-3}$	-0.219 ± 0.02
12	130	$(1.45\pm0.06)\times10^{-3}$	$(-1.17\pm0.16)\times10^{-3}$

Table 5.12 Estimated Activation Energy and Pre-exponential Constants and Associated 95% Confidence Intervals for Model 3 Using the Box-Kanemasu Method and DSC Data.

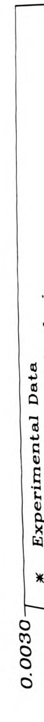
$\ln(A_1)$($\ln(s^{-1})$)	E_1 (kJ/mole)	Exp. Constant
10.63 ± 0.10	57.01 ± 0.29	$(-6.01\pm9.62)\times10^{-2}$

5.3 Estimation of Cure Kinetic Parameters of EPON 828/mPDA Epoxy Using Dielectric Data:

In this section, results are presented for the estimation of the kinetic parameters from dielectric data for the three models presented in eq.(3.1), (3.2) and (3.3) using the linear regression and Box-Kanemasu methods of estimation. In each case, the degree of cure was calculated from the log conductivity data obtained from isothermal experiments, and the 100% log conductivity value obtained from the dynamic experiments.

5.3.1 Estimation of the Kinetic Parameters from Dielectric data For Model 1:

The estimated linear regression curve and 95% confidence bands for the estimation of the rate constants from one isothermal dielectric experiment are shown in Figure 5.9. The estimated rate constants and 95% confidence intervals obtained using the linear regression method from each of the isothermal experiments are given in Table 5.13, and the resulting estimates of the Arrhenius constants are shown in Table 5.14. The associated estimates of the rate constants using the Box-Kanemasu method are shown in Table 5.15, and the Arrhenius constants obtained using this method are given in Table 5.16. The Arrhenius constants were obtained using all of the isothermal data as described for the DSC data.


0.0030
* Experimental Data

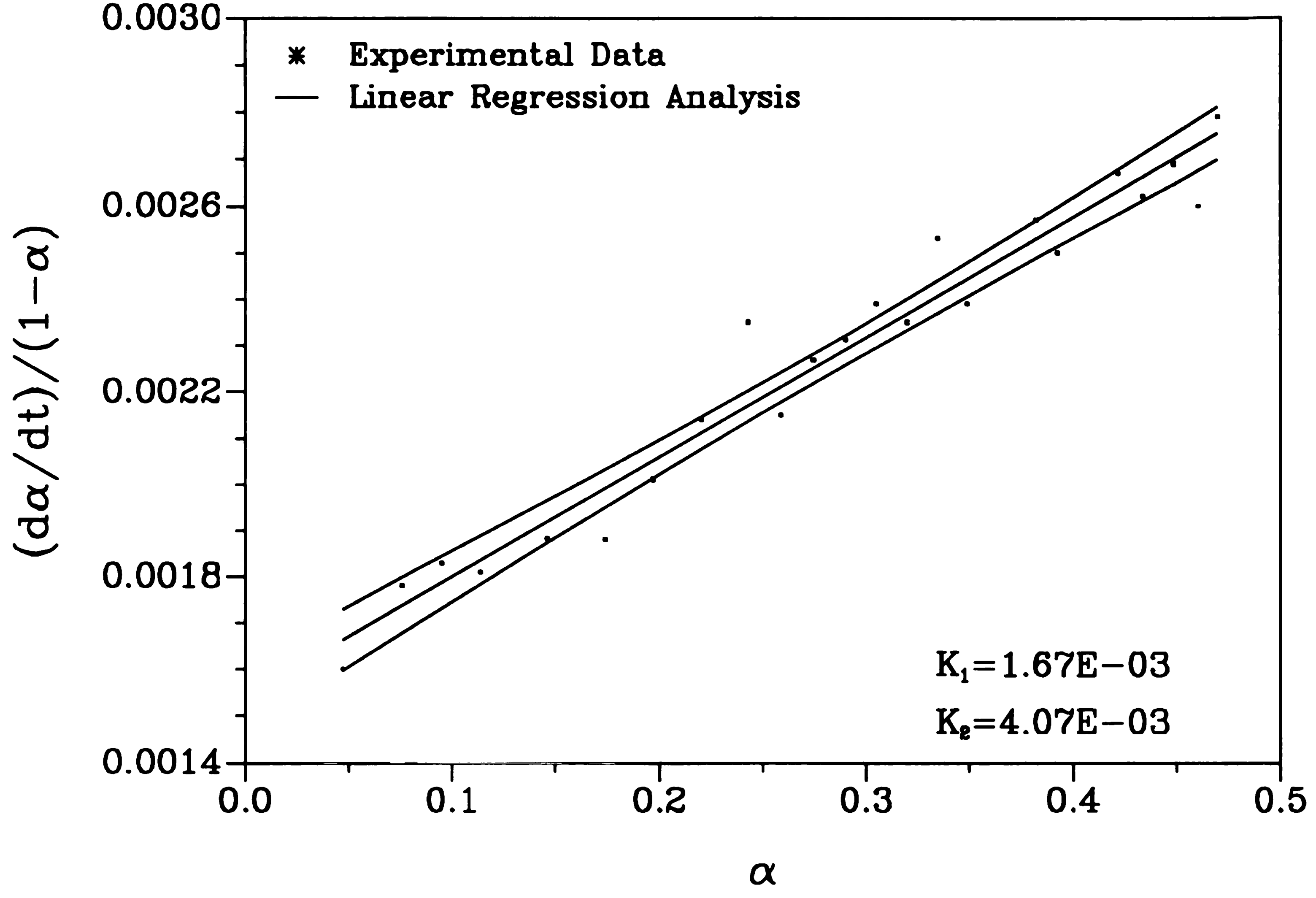


Figure 5.9 Estimation of the Rate Constants for Exp. 11 for Model 1 Using Dielectric Data.

Table 5.13 Estimated Rate Constants and Associated 95% Confidence Intervals for Model 1 Using Linear Regression Method and Dielectric Data.

Exper. No.	Temp. (°C)	Least Squares Method	
		K_1 (s^{-1})	K_2 (s^{-1})
1	70	$(4.25\pm0.36)\times10^{-5}$	$(4.52\pm0.23)\times10^{-4}$
2	70	$(3.78\pm0.29)\times10^{-5}$	$(3.54\pm0.21)\times10^{-4}$
3	70	$(3.32\pm0.41)\times10^{-5}$	$(2.57\pm0.17)\times10^{-4}$
4	80	$(1.79\pm0.27)\times10^{-4}$	$(7.92\pm0.17)\times10^{-4}$
5	80	$(2.06\pm0.31)\times10^{-4}$	$(5.88\pm0.19)\times10^{-4}$
6	80	$(1.35\pm0.23)\times10^{-4}$	$(6.90\pm0.23)\times10^{-4}$
7	120	$(6.27\pm0.29)\times10^{-4}$	$(2.59\pm0.14)\times10^{-3}$
8	120	$(5.76\pm0.31)\times10^{-4}$	$(3.04\pm0.19)\times10^{-3}$
9	120	$(6.78\pm0.25)\times10^{-4}$	$(2.67\pm0.17)\times10^{-3}$
10	130	$(1.07\pm0.12)\times10^{-3}$	$(2.75\pm0.16)\times10^{-3}$
11	130	$(1.67\pm0.17)\times10^{-3}$	$(4.07\pm0.27)\times10^{-3}$
12	130	$(7.89\pm0.09)\times10^{-4}$	$(3.89\pm0.26)\times10^{-3}$

Table 5.14 Estimated Activation Energy and Pre-exponential Constants and Associated 95% Confidence Intervals for Model 1 Using the Linear Regression Method and Dielectric Data.

$\ln(A_1)(\ln(s^{-1}))$	E_1 (kJ/mole)	$\ln(A^2)$ $(\ln(s^{-1}))$	E_2 (kJ/mole)
10.53±2.07	58.20±3.45	5.89±1.87	39.08±4.54

Table 5.15 Estimated Rate Constants for Model 1 and Associated 95% Confidence Intervals Using the Box-Kanemasu Method and Dielectric Data.

Exper. No.	Temp. (°C)	Box-Kanemasu Method	
		K_1 (s^{-1})	K_2 (s^{-1})
1	70	$(6.31\pm1.38)\times10^{-6}$	$(8.78\pm0.63)\times10^{-4}$
2	70	$(2.92\pm0.12)\times10^{-5}$	$(5.15\pm0.18)\times10^{-4}$
3	70	$(9.76\pm1.02)\times10^{-6}$	$(6.89\pm0.37)\times10^{-4}$
4	80	$(3.87\pm0.17)\times10^{-5}$	$(1.41\pm0.03)\times10^{-3}$
5	80	$(2.63\pm0.05)\times10^{-5}$	$(9.56\pm0.10)\times10^{-4}$
6	80	$(3.12\pm0.11)\times10^{-5}$	$(8.96\pm0.12)\times10^{-4}$
7	120	$(1.88\pm0.12)\times10^{-4}$	$(3.43\pm0.15)\times10^{-3}$
8	120	$(9.15\pm0.59)\times10^{-5}$	$(3.51\pm0.12)\times10^{-3}$
9	120	$(1.56\pm0.11)\times10^{-4}$	$(3.12\pm0.09)\times10^{-3}$
10	130	$(3.30\pm0.42)\times10^{-4}$	$(3.71\pm0.42)\times10^{-3}$
11	130	$(2.63\pm0.14)\times10^{-4}$	$(3.26\pm0.15)\times10^{-3}$
12	130	$(2.89\pm0.37)\times10^{-4}$	$(4.17\pm0.19)\times10^{-3}$

Table 5.16 Estimated Activation Energy and Pre-exponential Constants and Associated 95% Confidence Intervals for Model 1 Using the Box-Kanemasu Method and Dielectric Data.

$\ln(A_1)$($\ln(s^{-1})$)	E_1 (kJ/mole)	$\ln(A^2)$ ($\ln(s^{-1})$)	E_2 (kJ/mole)
3.87 ± 0.80	39.74 ± 1.50	5.17 ± 1.81	37.39 ± 5.17

5.3.2 Estimation of the Kinetic Parameters from Dielectric data For Model 2:

The rate constants and Arrhenius constants were estimated for Model 2 using both the linear regression and the Box-Kanemasu estimation methods. The estimates of the rate constants from each of the isothermal experiments using the linear regression method are shown in Table 5.17, and the resulting Arrhenius constants are shown in Table 5.18. The results from using the Box-Kanemasu estimation method are shown in Table 5.19 for the rate constants and in Table 5.20 for the Arrhenius constants. Once again, the Arrhenius constants were obtained using all of the isothermal data in the estimation procedure.

Table 5.17 Estimated Rate Constants and Associated 95% Confidence Intervals
for Model 2 Using the Linear Regression Method
And Dielectric Data.

Exper. No.	Temp. (°C)	Least Squares Method	
		K_1 (s^{-1})	K_2 (s^{-1})
1	70	$(5.32\pm2.36)\times10^{-5}$	$(9.65\pm1.23)\times10^{-4}$
2	70	$(1.56\pm0.81)\times10^{-5}$	$(6.12\pm2.07)\times10^{-4}$
3	70	$(7.98\pm1.99)\times10^{-5}$	$(2.57\pm0.17)\times10^{-4}$
4	80	$(6.95\pm3.27)\times10^{-5}$	$(1.56\pm0.97)\times10^{-3}$
5	80	$(1.02\pm.56)\times10^{-4}$	$(7.54\pm2.03)\times10^{-4}$
6	80	$(1.23\pm0.74)\times10^{-4}$	$(9.77\pm2.88)\times10^{-4}$
7	120	$(1.99\pm.82)\times10^{-4}$	$(7.26\pm2.41)\times10^{-3}$
8	120	$(4.67\pm1.94)\times10^{-4}$	$(2.97\pm1.23)\times10^{-3}$
9	120	$(1.11\pm2.23)\times10^{-3}$	$(1.75\pm0.84)\times10^{-3}$
10	130	$(1.81\pm1.01)\times10^{-3}$	$(3.01\pm11.13)\times10^{-3}$
11	130	$(1.67\pm0.17)\times10^{-3}$	$(2.67\pm1.74)\times10^{-3}$
12	130	$(6.34\pm2.63)\times10^{-4}$	$(3.19\pm1.43)\times10^{-3}$

Table 5.18 Estimated Activation Energy and Pre-exponential Constants and Associated 95% Confidence Intervals for Model 2 Using the Linear Regression Method and Dielectric Data.

$\ln(A_1)(\ln(s^{-1}))$	E_1 (kJ/mole)	$\ln(A^2)$ $(\ln(s^{-1}))$	E_2 (kJ/mole)
7.88±4.07	88.20±19.45	12.66±5.32	31.72±14.57

Table 5.19 Estimated Rate Constants and Associated 95% Confidence Intervals for Model 2 Using the Box-Kanemasu Method and Dielectric Data.

Exper. No.	Temp. (°C)	Box-Kanemasu Method	
		K_1 (s^{-1})	K_2 (s^{-1})
1	70	$(-4.05\pm2.01)\times10^{-3}$	$(2.76\pm1.23)\times10^{-2}$
2	70	$(-1.91\pm1.02)\times10^{-5}$	$(7.69\pm1.96)\times10^{-3}$
3	70	$(7.32\pm1.86)\times10^{-6}$	$(5.75\pm2.05)\times10^{-3}$
4	80	$(-6.48\pm3.75)\times10^{-3}$	$(3.40\pm1.98)\times10^{-2}$
5	80	$(4.75\pm6.55)\times10^{-8}$	$(1.15\pm0.40)\times10^{-2}$
6	80	$(5.69\pm3.72)\times10^{-8}$	$(2.09\pm0.76)\times10^{-2}$
7	120	$(-5.92\pm3.89)\times10^{-3}$	$(2.65\pm0.25)\times10^{-2}$
8	120	$(1.45\pm1.99)\times10^{-7}$	$(1.19\pm0.81)\times10^{-2}$
9	120	$(8.39\pm5.41)\times10^{-7}$	$(2.51\pm0.67)\times10^{-2}$
10	130	$(1.10\pm0.87)\times10^{-5}$	$(2.78\pm2.42)\times10^{-3}$
11	130	$(2.06\pm3.71)\times10^{-7}$	$(1.33\pm1.08)\times10^{-3}$
12	130	$(6.71\pm3.06)\times10^{-6}$	$(2.61\pm1.12)\times10^{-2}$

Table 5.20 Estimated Activation Energy and Pre-exponential Constants and Associated 95% Confidence Intervals for Model 2 Using the Box-Kanemasu Method and Dielectric Data.

$\ln(A_1)(\ln(s^{-1}))$	E_1 (kJ/mole)	$\ln(A^2)$ $(\ln(s^{-1}))$	E_2 (kJ/mole)
8.34±3.92	76.38±17.81	10.82±4.82	34.10±13.91

5.3.3 Estimation of the Kinetic Parameters from Dielectric Data for Model 3:

The results of applying the linear regression method to Model 3 with dielectric data are given in Table 5.21 for the rate and exponential constants and in Table 5.22 for the Arrhenius constants. The analogous parameter estimates obtained using the Box-Kanemasu method are shown in Tables 5.23 and 5.24.

Table 5.21 Estimated Rate Constant and Exponential Constant and Associated 95% Confidence Intervals for Model 3 Using Linear Regression Method and Dielectric Data.

Exper. No.	Temp. (°C)	Least Squares Method	
		K_1 (s^{-1})	Exp. constant
1	70	$(5.62\pm0.71)\times10^{-5}$	$(4.19\pm1.95)\times10^{-4}$
2	70	$(1.98\pm0.79)\times10^{-5}$	$(6.87\pm2.12)\times10^{-4}$
3	70	$(8.65\pm1.13)\times10^{-5}$	$(2.09\pm0.85)\times10^{-4}$
4	80	$(1.22\pm0.69)\times10^{-4}$	$(6.73\pm2.87)\times10^{-4}$
5	80	$(6.83\pm2.01)\times10^{-5}$	$(9.34\pm3.23)\times10^{-5}$
6	80	$(1.45\pm0.61)\times10^{-4}$	$(7.36\pm2.87)\times10^{-4}$
7	120	$(4.20\pm1.23)\times10^{-4}$	$(3.34\pm1.95)\times10^{-5}$
8	120	$(3.58\pm1.39)\times10^{-4}$	$(8.32\pm2.49)\times10^{-5}$
9	120	$(8.29\pm3.10)\times10^{-4}$	$(7.35\pm3.08)\times10^{-4}$
10	130	$(6.02\pm1.56)\times10^{-4}$	$(8.34\pm2.47)\times10^{-5}$
11	130	$(7.48\pm1.09)\times10^{-4}$	$(2.39\pm1.21)\times10^{-4}$
12	130	$(1.12\pm0.71)\times10^{-3}$	$(6.37\pm2.38)\times10^{-5}$

Table 5.22 Estimated Activation Energy, Pre-exponential, and Exponential Constants and Associated 95% Confidence Intervals for Model 3 Using the Linear Regression Method and Dielectric Data.

$\ln(A_1)(\ln(s^{-1}))$	E_1 (kJ/mole)	Exp. Constant
9.03 ± 3.61	41.82 ± 13.91	$(4.49\pm1.97)\times10^{-4}$

Table 5.23 Estimation of the Rate Constant and Exponential Constant and Associated 95% Confidence Intervals for Model 3 Using Box-Kanemasu Method and Dielectric Data.

Exper. No.	Temp. (°C)	Least Squares Method	
		K_1 (s^{-1})	Exp. constant
1	70	$(6.91\pm0.30)\times10^{-5}$	$(7.80\pm1.73)\times10^{-4}$
2	70	$(3.45\pm0.62)\times10^{-5}$	$(8.31\pm3.16)\times10^{-4}$
3	70	$(7.32\pm0.41)\times10^{-5}$	$(1.48\pm0.79)\times10^{-4}$
4	80	$(1.04\pm0.05)\times10^{-4}$	$(5.22\pm1.93)\times10^{-4}$
5	80	$(8.17\pm0.56)\times10^{-5}$	$(6.18\pm1.45)\times10^{-5}$
6	80	$(4.61\pm0.29)\times10^{-5}$	$(2.98\pm1.28)\times10^{-5}$
7	120	$(5.19\pm0.36)\times10^{-4}$	$(7.48\pm2.52)\times10^{-4}$
8	120	$(2.81\pm0.19)\times10^{-4}$	$(8.45\pm3.19)\times10^{-5}$
9	120	$(4.82\pm0.49)\times10^{-4}$	$(9.12\pm2.91)\times10^{-5}$
10	130	$(5.92\pm0.37)\times10^{-4}$	$(9.13\pm2.43)\times10^{-4}$
11	130	$(5.06\pm0.39)\times10^{-4}$	$(8.07\pm2.73)\times10^{-4}$
12	130	$(6.19\pm0.41)\times10^{-3}$	$(1.13\pm0.31)\times10^{-3}$

Table 5.24 Estimated Activation Energy, Pre-exponential, and Exponential Constants and Associated 95% Confidence Intervals for Model 3 Using the Box-Kanemasu Method and Dielectric Data.

$\ln(A_1)(\ln(s^{-1}))$	E_1 (kJ/mole)	Exp. Constant
11.23 ± 3.45	34.29 ± 12.17	$(5.91\pm2.18)\times10^{-4}$

5.4 Comparison of Results:

The first objective of this research work is to analyze the DSC and dielectric experimental techniques. The data from these two experimental procedures was used to estimate the kinetic parameters using two estimation methods and three kinetic models. The results obtained for the Arrhenius constants are compared in Tables 5.25, 5.26, and 5.27 for the parameters associated with Models 1, 2, and 3, respectively. The estimated standard deviation values shown in each table are calculated from the residuals as follows:

$$\text{Standard Deviation} = s = \left(\frac{\sum_{i=1}^{n} (Y_{o,i} - Y_{p,i})^2}{N-p} \right)^{1/2} \qquad (5.1)$$

The estimated standard deviations values shown in the above tables were smaller for the DSC results than for the dielectric results. When comparing the confidence intervals of the estimated parameters in Tables 5.25-5.27, the confidence intervals resulting from the use of DSC data were consistently smaller than those found from the use of dielectric data. The DSC results were expected to be more accurate than the dielectric results since the data collected with the DSC (Figure 5.5) have less variability than the dielectric data, and there were more measurements associated with each DSC experiment than there were for the dielectric experiments (Figure 5.9).

Two methods of estimations were used in this research study: the linear regression method and the Box-Kanemasu minimization method. The second objective of this discussion is to examine the difference between the results obtained using these two methods. In comparing the estimated parameters using the Box-Kanemasu method

Table 5.25 Activation Energy Constants, E_1 and E_2, and Pre-Exponential Factors, A_1 and A_2, For Model 1 (eq.(3.1) and eq.(3.4)) For Both DSC and Dielectrometry Using the Least Square and Box-Kanemasu Methods.

Exp. procedure (temp.,°C)	E_1 (kJ/mole)	E_2 (kJ/mole)	$\ln(A_1)$ $\ln(s^{-1})$	$\ln(A_2)$ $\ln(s^{-1})$	Standard Deviation	Reference (est. method)
Isothermal DSC (70-130)	68.19±2.81	51.09±3.98	12.93±1.57	10.70±1.47	6.75×10^{-2}	this study (least square)
Isothermal DSC (70-130)	68.36±1.60	38.69±1.21	14.26±0.53	5.45±0.38	5.33×10^{-2}	this study (Box-Kan.)
Iso. Dielectric (70-130)	58.20±3.45	39.08±4.54	10.53±2.07	5.89±1.87	0.19	this study (least square)
Iso. Dielectric (70-130)	39.74±1.45	37.39±5.17	3.87±0.80	5.17±1.81	5.97×10^{-2}	this study (Box-Kan.)
Isothermal DSC (60-110)	55.8±5.8	49.2±2.1	9.4±2.0	9.4±0.7		Scott, 1989 (least square)
Isothermal DSC (90-170)	65	46	11.8	not given		Ryan and Dutta (1979)
Isothermal DSC (70-140)	62	48	10.6	9.1		Kamal et al. (1973)

Table 5.26 Activation Energy Constants, E_1 and E_2, and Pre-Exponential Factors, A_1 and A_2, For Model 2 (eq.(3.2) and eq.(3.4)) For Both DSC and Dielectrometry Using the Least Square and Box-Kanemasu Methods.

Exp. procedure (temp.,°C)	E_1 (kJ/mole)	E_2 (kJ/mole)	$\ln(A_1)$ $\ln(s^{-1})$	$\ln(A_2)$ $\ln(s^{-1})$	Standard Deviation	Reference (est. method)
Isothermal DSC (70-130)	68.36±3.80	38.69±1.21	14.26±0.53	5.45±0.38	7.15×10^{-2}	this study (least square)
Isothermal DSC (70-130)	67.20±6.17	55.05±3.96	12.88±2.04	12.09±0.32	6.51×10^{-2}	this study (Box-Kan.)
Iso. Dielectric (70-130)	88.20±19.45	31.72±14.57	7.88±4.07	12.66±5.32	0.27	this study (least square)
Iso. Dielectric (70-130)	76.38±17.81	34.10±13.91	8.34±3.92	10.82±4.82	0.25	this study (Box-Kan.)
Isothermal DSC (60-110)	64.5±4.9	50.6±2.0	12.1±1.7	10.6±0.7		Scott, 1989 (least square)
Isothermal DSC (60-130)	81	48	16.0	9.5		Sourour and Kamal (1976)

Table 5.27 Activation Energy Constant, E_1, Pre-Exponential Factor, A_1, and Exponential Constant For Model 3 (eq.(3.3) and eq.(3.4)) For Both DSC and Dielectrometry Using the Least Square and Box-Kanemasu Methods.

Exp. procedure (temp.,°C)	E_1 (kJ/mole)	$\ln(A_1)$ $\ln(s^{-1})$	Exponential Constant	Standard Deviation	Reference (est. method)
Isothermal DSC (70-130)	70.82 ± 17.53	15.11 ± 5.69	-1.58 ± 0.092	0.11	this study (least square)
Isothermal DSC (70-130)	57.01 ± 0.288	10.63 ± 0.102	$(-6.01 \pm 9.62) \times 10^{-2}$	4.76×10^{-2}	this study (Box-Kan.)
Isothermal Dielectric (70-130)	41.82 ± 13.91	9.03 ± 3.61	$(4.49 \pm 1.97) \times 10^{-4}$	0.184	this study (least square)
Isothermal Dielectric (70-130)	34.29 ± 12.17	11.23 ± 3.45	$(5.91 \pm 2.18) \times 10^{-4}$	0.159	this study (Box-Kan.)
Isothermal DSC (60-110)	56.1 ± 4.9	16.2 ± 0.8	-1.74 ± 0.36		Scott, 1989 (least square)
Dynamic DSC (115-130)	50-63	8-12	0.9-1.3		Prime (1970,1973)

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with those obtained using the linear regression method in Tables 5.25-5.27, the Box-Kanemasu method generally resulted in smaller 95% confidence regions than the linear regression method. The exceptions to this observation are the Arrhenius parameters associated with the second rate constant in Model 2. The standard deviations associated with the Box-Kanemasu method were also smaller than those obtained using linear regression.

The third objective of this research study is to investigate the three different kinetic models presented in Chapter 3. The first and most obvious task is to determine if the estimated parameters are physically reasonable. In this case, it is required that all of the estimated parameters be positive. The results for Model 1 and Model 2 in Tables 5.25 and 5.26 satisfy this criterion; however, the exponential constant in Model 3 was estimated to be a negative value using DSC data. This infers a negative order of reaction, which does not have a physical meaning. In addition, the exponentials estimated from the dielectric data were found to be very small which indicates that the order of reaction is near zero. Based on these observations, it was determined that Model 3 is inappropriate to use in describing the cure kinetics of the EPON 828/mPDA resin. Note that this is the only model that does not include autocatalyzation in the mechanism.

Both Model 1 and Model 2 have positive parameters estimates, and therefore, both are physically reasonable. To determine the model which most accurately describes the curing process, the standard deviations of the models were compared. The standard deviations resulting from the use of Model 1 were found to be smaller than those calculated for Model 2. This is an indication that Model 1 might be a better model to describe the curing process for this particular resin than Model 2. It should be noted, however, that the differences between the two models are small. The first model does have the additional advantage in that it is simpler, and therefore, the calculations associated with the estimation procedure are simplified and reduced.

Selecting Model 1 as the most appropriate model for the resin under consideration, the magnitude of the parameter estimates from the different experimental methods and estimates procedures and from previous studies are now compared. The results associated with the first rate constant (E_1 and $\ln(A_1)$) obtained using different experimental procedures and different estimation methods have the largest variability. This is to be expected, since the first rate constant is associated with the initial stages of the curing process when experimental errors tend to be the greatest. These errors arise from the assumption that the sample is instantaneously at the desired curing temperature at the beginning of the isothermal experiments.

It is interesting to note that the results obtained for the Arrhenius constants associated with the second rate constant (E_2 and $\ln(A_2)$) in Model 1 are statistically equivalent for the Box-Kanemasu method using both DSC and dielectric data and the linear regression method using the dielectric data. These parameter estimates are significantly lower than those obtained using DSC and linear regression. This includes not only the results from this study, but also the results from the three previous studies which were also found using DSC and the linear regression method. The agreement between the results for E_2 and $\ln(A_2)$ is significant, in that although the use of DSC data results has less variability in the estimated parameters, equivalent results were obtained for the DSC and dielectric data if the Box-Kanemasu estimation method is utilized. This is important because, unlike DSC experiments, large samples can be used in dielectric studies which allows for the investigation of the curing process in nonhomogeneous materials such as fiber composite materials.

Finally, the best parameter estimates were selected from the experimental data and estimation method which provided the estimates with the smallest confidence intervals and which resulted in the smallest standard deviation. From Table 5.25 for Model 1, the "best" estimates resulted from the use of DSC data and the Box-Kanemsu minimization method. This was to be expected since, as stated previously, the DSC data had less variability, and the Box-Kanemsu method generally resulted in smaller confidence regions for the estimated parameters.

Chapter 6

Conclusions

In this study, the kinetic parameters associated with the curing of EPON 828-mPDA resin were determined for three different kinetic models from both DSC and dielectric experimental data using two different estimation procedures. The two estimation procedures were the linear regression method, which is the most commonly used method, and the Box-Kanemasu method, which has not been used before in this application.

The following conclusions were drawn from this study:

1. From the analysis of the sensitivity coefficients, the use of the degree of cure, α, as the measured variable provides better parameter estimates than the use of the degree of cure rate ($d\alpha/dt$).
2. The parameters estimated using dielectric data have more variability than those estimated using DSC data.
3. The use of the third kinetic model (Model 3) resulted in physically unreasonable estimates for the order of reaction, and therefore, it is determined to be inappropriate in describing the curing reaction associated with the epoxy resin under consideration.
4. The Box-Kanemasu method generally resulted in smaller confidence intervals and smaller standard deviations for each model than the linear regression method.
5. The use of the first kinetic model (Model 1) with DSC data and the Box-Kanemasu method provided the best description of the curing process for the EPON 828-mPDA epoxy.

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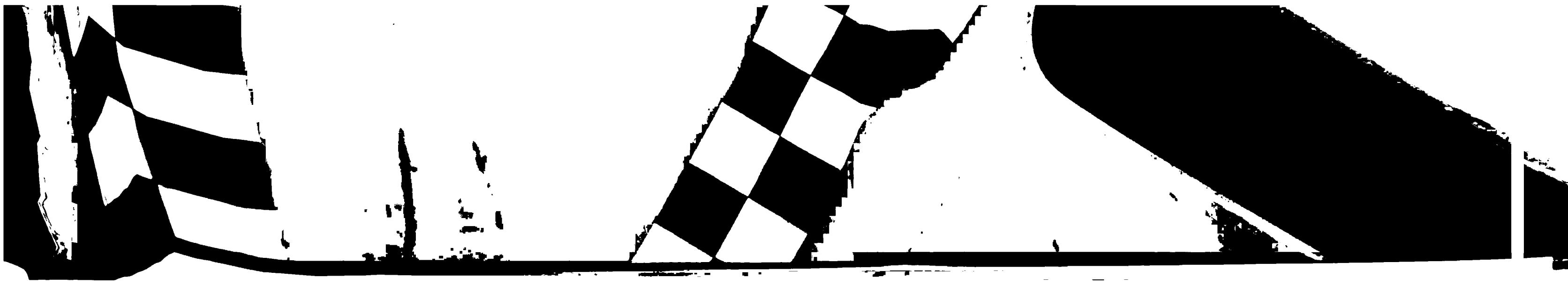
Chapter 7

Recommendations

Based on the results obtained and also the difficulties encountered during this study, future recommendations can be introduced:

1. The termination of the kinetic controlled process is arbitrary and dependent on many factors such as curing temperature. Consequently, a systematic methodology to determine the termination of the kinetic reaction is needed.
2. A general model that describes the whole curing process, including the diffusion controlled part, should be developed.
3. In case of correlated residuals, the model might need to be modified or altered. Specifically, an investigation of the residuals sequentially during the estimation procedure can give insight into the appropriateness of the model.



APPENDIX A

Perk

1. D

APPENDIX A

Perkin-Elmer DSC (Perkin-Elmer DSC Operator's Manual, 1989):

1. DSC 7 Differential Scanning Calorimeter:

DSC type	Power compensated temperature null principle. Measures energy directly, Not differential temperature.
DSC cell	Independent dual furnaces constructed of platinum-iridium alloy with independent platinum resistance heaters and temperature sensors.
Calorimeter Precision	Better than ±0.1%
Temperature Precision	±0.1°C
Temperature Accuracy	±0.1°C
Temperature Display	0.1° increments
Heating & Cooling rates	0.1°C/min to 200°C/min in 0.1°C increments.
Temperature Range	Standard unit allows operation from ambient to 730°C. With operational accessories, the range may be extended to -170°C.
Temperature Sensors	Distributed, platinum resistance thermometers.
Atmosphere	Static or dynamic including nitrogen, argon, helium, carbon dioxide, air, oxygen or other inert or non-corrosive gases.
Sample Type	Solids, liquids, powders, films or fibers.
Sample Size	Precision and accuracy are based on running a 4-8 mg sample of indium at

2. TA

3.

4

5°C/min on a calibrated instrument. It is recommended that the sample does not exceed 15 mg.

2. TAC 7/PC Thermal Analysis Controller:

General	The TAC 7/PC is the intelligent microprocessor controller that links the PC to the thermal analysis module.
Microprocessor	High speed microprocessor control of all functions.
Communications Ports	Two RS-232C communications ports, an analog control port, and a digital control port.
Diagnostics	Built-in diagnostics continuously monitor and analyze all system functions.

3. GSA 7 Gas Selector Accessory:

General	The GSA permits an automatic switching of purge gases at operator selected intervals. Compatible with all thermal analysis instrument modules.
Type	Automatic computer controlled gas switching device which is directly controlled gas switching device which is directly controllable through the PC.

4. Graphics Plotters:

General	High resolution alphanumeric X-Y printer/plotter with graphics.
Operation	Multiple pen operation for generating multi-color plots.
Scaling	Automatic scaling performed and optimized by the PC.
Hard Copy	Publication quality data presentation and results.

APPENDIX B

APPENDIX B

The Eumetric System III Microdielectrometer:(Micromet Instrument, 1988):

1. System III Microdielectrometer:

Dimensions (L×W×H)	19.5"×17.5"×7"
Weight	35 lbs. (16 kg)
Power	120 V AC, 60 Hz, 3 Amps grounded with external switch for 220 V AC and 50 Hz.
Signal Frequency Range	0.001 to 100,000 Hz in one hundred and seven discrete steps.
Amplitude Measurement Range	-50 to 1 dB.
Amplitude Meas. Accuracy	0.1 dB relative to 2.0 V peak to peak.
Phase Measurement Range	0.0 to ±180°.
Phase Measurement Accuracy	0.1° at frequencies lower than 10,000 Hz, 1.0° at frequencies higher than 10,000 Hz.
External Controls	Power ON/OFF and RESET; Interface Type Select; Configuration Parameter Select, Ramp Up, Ramp Down, Digit Select, Enter, Measurement Select, Enter, Measurement Select, Start.
Front Panel Functions	Full single measurements of E'/E", Gain-Admittance/Phase, Temperature, Capacitance/Resistance, and Offset/Range. Selection of the sensor Interface, Configuration Parameters (measurement excitation frequency, multiplexer channel) and measurements to be made are programmed and initiated from the front channel.
Controller Interface	RS232C serial Interface is configurated as a data terminal equipment (DTE).

2. Eight Channel Multiplexer:

Dimensions	18.3"×10.3"×4.1"
weight	10 lbs.
Channel Options	Low, Mid, High, or Ceramic with high density cable.

3. Eumetric Programmable Oven:

Dimensions:	
Chassis	18.5"×12.25"×6"
External Oven Stage	4.25" diameter×7.5"
Internal Oven Stage	2.25" diameter×2.75"
Maximum Sample Size	2.25" diameter×0.875"
Weight	15 lbs.
Power	110 V AC, 60 Hz, 5 amps, grounded with external switch for 220V, 50/60 Hz.
Temperature Range	-150°C to 500°C (-238°F to 932°F)
Heating Rate	0 to 5°C/min for an overshoot less than 2°C, maximum heating rate 25°C/min
External Controls	Power ON/OFF. With 359L, a switch to indicate the sensor in use (Ceramic or Ceramic Parallel Plate) is also located on the front of the oven.
Oven Controller	Controller is an LFE Instruments Division Model 0211. This three-mode PID controller has an eight key operator interface and an alphanumeric display with ON/OFF, time proportional or analog output. These keys are preset at micromet instruments, Inc. and are not used during normal operation.

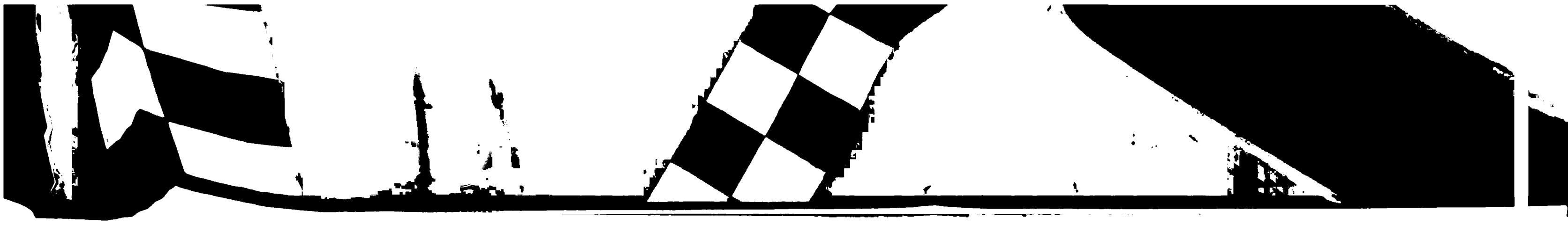
4. Low Conductivity (Integrated Circuit) Sensor:

Sensor Dimensions	14"×0.375"×0.02"
Active Face Dimensions	0.2"×0.1"×0.01"
Depth of Recess	0.004"
Measurement Values	

Log Conductivity	-16 to -5 (Siemens/cm)
Log Loss Factor	-2 to 3
Permitivity	1 to 40
temperature	-100°C to 250°C
temperature accuracy	±3°C
Pressure Limitations	to ~200 psi without support
Applications	Epoxy, BMI, Silicone, Thermoplastics, Thermosets, Rubber, Urethane, RIM, Composites, Polyester.

5. Eumetric System III Software:

The Eumetric System III control software (310d) and the fast measurement module (313D) grants the user a complete control over the operation of the system III microdielectrometer and its different configurations for the use in many applications. A flow chart of the a sample program is presented in figure in order to explain the way the software works.



APPENDIX C

1. B

```
CCC
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C  V
C
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 C
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```

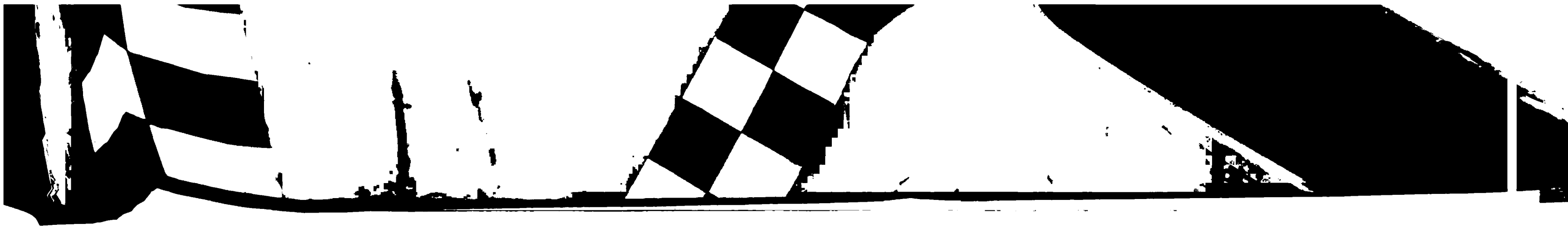

APPENDIX C

1. Box-Kanemasu Method Computer Program (Beck, 1991):

```
      PROGRAM NLINA
CCCCCCCCC            PROGRAM DESCRIPTION              CCCCC
C                                            C
C          PROGRAM NLINC
C   WRITTEN BY JAMES V. BECK                              C
C   LAST REVISED MAY 1, 1991
C***************************************************************C
C                                            C
CVCCCCCCCC          VARIABLE IDENTIFICATION           CCCCCCCC
C                                            C
C                                            C
C***************************************************************C
C                                            C
CDCCCCCCCC             DIMENSION BLOCK            BLOCK 0000
C                                            C
C
 C
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION T(1000,5),Y(1000),SIG2(1000),B(5),Z(5),A(5),BS(5),
     1VINV(5,5),BSS(5),CG(5),BSV(5),R(5,5),EXTRA(20),ERR(1000)
     1, PS(5,5),P(5,5),PSV(5,5),
     1 XTX(5,5),XTY(5)
      CHARACTER*40 DFILE,OUTFIL
C                                            C
C***************************************************************C
C                                            C
COCCCCCCCC              COMMON BLOCK              BLOCK 0100
C                                            C
      COMMON T,Z,BS,I,ETA,PS,P,B,A,Y,SIG2,MODL,VINV,NP,EXTRA
      COMMON/ERROR/ERR
C                                            C
C                                            C
C***************************************************************C
C                                            C
CACCCCCCCC                DATA BLOCK            BLOCK 0200
C                                            C
      DATA EPS,EPSS,IIN,IOUT/1.0D-30,0.0001D+0,5,7/
C                                            C
C***************************************************************C
C                                            C
CICCCCCCCC          INITIALIZATION BLOCK          BLOCK 0400
C                                            C
      WRITE(*,*)'ENTER THE NAME OF THE DATA FILE'
      READ(*,'(A40)') DFILE
```

```
C
C***
C
CPC
C
C --
C

200








C -
C -
C -
C



C


15
C

C
```

```
      OPEN(8,FILE=DFILE)
      WRITE(*,*)'ENTER THE NAME OF THE OUTPUT FILE'
      READ(*,'(A40)') OUTFIL
      OPEN(7,FILE=OUTFIL)
C                                                                  C
C*****************************************************************C
C                                                                  C
CPCCCCCCCC          PROCESS BLOCK                  BLOCK 0500
C                                                                  C
C --- START INPUT
C     BLOCK 1
      WRITE(7,*)'BEGIN LISTING INPUT QUANTITIES'
200   READ(8,*) N,NP,NT,ITMAX,MODL,IPRINT
      WRITE(7,*)
      WRITE(7,*)'BLOCK 1'
      WRITE(7,*)'N = NO. DATA POINTS, NP = NO. PARAMETERS'
      WRITE(7,*)'NT = NO. OF INDEPENDENT VARIABLES'
      WRITE(7,*)'ITMAX = MAXIMUM NO. OF ITERATIONS'
      WRITE(7,*)'MODEL = MODEL NUMBER, IF SEVERAL MODELS IN SUBROUTINES:
     1 MODEL AND SENS'
      WRITE(7,*)'IPRINT = 1 FOR USUAL PRINTOUTS, 0 FOR LESS'
      WRITE(7,*)
       IF(N.LE.0) THEN
        STOP
      END IF
      WRITE(*,'(/,9X,"N",8X,"NP",8X,"NT",5X,"ITMAX",5X,
     +"MODEL",4X,"IPRINT")')
      WRITE(*,'(7I10)') N,NP,NT,ITMAX,MODL,IPRINT
      WRITE(7,'(/,9X,"N",8X,"NP",8X,"NT",5X,"ITMAX",5X,
     +"MODEL",4X,"IPRINT")')
      WRITE(7,'(7I10)') N,NP,NT,ITMAX,MODL,IPRINT
      IOPT=0
C --- IF IOPT=0 THEN ON THE 2ND AND SUCCEEDING STACKED CASES, THE DATA IS
C --- NOT REPRINTED.
C --- IF IPRINT=1, EXTRA PRINT OUT OF ETA, RESIDUALS B(1),... ARE GIVEN.
C     BLOCK 2
      WRITE(7,*)
      WRITE(7,*)'BLOCK 2'
      WRITE(7,*)'B(1),B(2),..,B(NP) ARE INITIAL PARAMETER ESTIMATES'
      WRITE(7,*)
      READ(8,*)(B(I),I=1,NP)
      WRITE(7,'(10X,"B(",I1,") = ",F16.5)') (I,B(I),I=1,NP)
C
      DO 150 J1=2,5
       BS(J1) = 0
150    CONTINUE
C
      IF(IOPT.LE.0) THEN
C         BLOCK 3
      WRITE(7,*)
      WRITE(7,*)'BLOCK 3'
      WRITE(7,*)'J =  DATA POINT INDEX,  Y(J)  = MEASURED VALUE'
```

```
 W
 W
 W
  V
+,6
  I



10
  E
C
313




2
C
C
C
C
C
C
6
C
C
ALL
C
C

 88
 C



 89

 C
 C
 C
```

```
      WRITE(7,*)'SIGMA(J) = STANDARD DEVIATION OF Y(J)'
      WRITE(7,*)'T(J,1) = FIRST INDEPENDENT VARIABLE'
      WRITE(7,*)
        WRITE(7,'(/,9X,''J'',6X,''Y(J)'',3X,''SIGMA(J)'',6X,''T(J,1)''
     +,6X,''T(J,2)'')')
        DO 10 I2=1,N
          READ(8,*)J,Y(J),SIG2(J),(T(J,KT),KT=1,NT)
          WRITE(7,'(I10,7F10.5)') J,Y(J),SIG2(J),(T(J,KT),KT=1,NT)
          SIG2(J) = SIG2(J)*SIG2(J)
10    CONTINUE
      END IF
C
313   DO 2 IP=1,NP
       DO 2 KP=1,NP
         PS(KP,IP) = 0
         P(KP,IP) = 0
2     CONTINUE
C      WRITE(7,'(/,5X,''P(1,KP)'',9X,''P(2,KP)'',9X,''P(3,KP)'',9X,
C     +''P(4,KP)'',9X,''P(5,KP)'')')
C      DO 6 IP=1,NP
C
C        READ(8,*)(PS(IP,KP),KP=1,NP)
C        WRITE(7,'(5D16.5)') (PS(IP,KP),KP=1,NP)
6     CONTINUE
C      BLOCK  4
C        BELOW IS TO INTRODUCE NONINFORMATIVE 'PRIOR INFORMATION'.  IT JUST
ALLOWS
C      US TO START WITH ONE MEASUREMENT EVEN THOUGH MORE PARAMETERS.
C      IT ALSO PUTS SOME BUFFERING IN THE INITIAL ESTIMATES.
      DO 88 IP=1,NP
88    PS(IP,IP)=B(IP)*B(IP)
C 88     PS(IP,IP)=B(IP)*B(IP)*1.0D+6
      READ(8,*)IEXTRA
      WRITE(7,*)'INITIAL P MATRIX'
      DO 89 IP=1,NP
      WRITE(7,*)(PS(IP,III),III=1,NP)
 89   CONTINUE

C      IEXTRA=0 FOR NO EXTRA INPUT WHICH COULD BE FOR CONSTANTS
C      IN MODELS
C      =1 FOR ONE INPUT, NAMELY: EXTRA(1), ETC.
      WRITE(7,*)
      WRITE(7,*)'BLOCK 4'
      WRITE(7,*)'IEXTRA = NO. OF EXTRA(I) PARAMETERS, 0 IF NONE'
      WRITE(7,*)
      WRITE(7,'(10X,''IEXTRA = '',I10)')IEXTRA
      IF(IEXTRA .LT. 1) GOTO 21
      WRITE(7,*)
      WRITE(7,*)'BLOCK 5'
      WRITE(7,*)'EXTRA(1),... ARE EXTRA CONSTANTS USED AS DESIRED'
      WRITE(7,*)
      READ(8,*)(EXTRA(IE),IE=1,IEXTRA)
```

```
      WRITE(7,'("EXTRA(",I2,") = ",F16.5)') (IE,EXTRA(IE),IE=1
     1,IEXTRA)
   21 CONTINUE
C
C — ADD BLANK CARD AFTER LAST INPUT CARD
C —END INPUT
      WRITE(7,*)'END INPUT QUANTITIES - - BEGIN OUTPUT CALCULATIONS'
      WRITE(7,*)
      WRITE(7,*)'SY =  SUM OF SQUARES FOR PRESENT PARAMETER VALUES'
      WRITE(7,*)'SYP = SUM OF SQUARES FOR GAUSS PARAMETER VALUES, SHOULD
     1 BE SMALLER THAN SY'
      WRITE(7,*)'      SYP DECREASES TOWARD A POSITIVE CONSTANT'
      WRITE(7,*)'G =   MEASURE OF THE SLOPE, SHOULD BECOME SMALLER AS
     1ITERATIONS PROCEED'
      WRITE(7,*)'      G SHOULD APPROACH ZERO AT CONVERGENCE'
      WRITE(7,*)'H =   FRACTION OF THE GAUSS STEP, AS GIVEN BY THE
     1BOX-KANEMASU METHOD'
      WRITE(7,*)
      WRITE(7,*)
      DO 18 IL=1,NP
        BS(IL)=B(IL)
       CG(IL) = 0
18     CONTINUE
      DO 19 IP=1,NP
        XTY(IP)=0.0D+0
        DO 19 KP=1,NP
          P(KP,IP) = PS(KP,IP)
          XTX(IP,KP)=0.0D+0
19     CONTINUE
      I = 0
      MAX = 0
C
99     MAX = MAX + 1
C — START BASIC LOOP GIVES B(I) AND SY
C
      SY = 0.0D+0
      DO 100 I3=1,N
        I = I3
        CALL SENS
        CALL MODEL
        RISD = Y(I)-ETA
        SY = SY + RISD*RISD/SIG2(I)
        SUM = 0.0D+0
        DO 20 K=1,NP
          XTY(K)=XTY(K)+Z(K)*RISD/SIG2(I)
          DO 20 L=1,NP
            SUM = SUM + Z(L)*P(K,L)*Z(K)
            XTX(K,L)= XTX(K,L) + Z(L)*Z(K)/SIG2(I)
20      CONTINUE
        DELTA = SIG2(I) + SUM
        DO 29 JJ=1,NP
          A(JJ) = 0.0D+0
```

```
29   CONTINUE
     DO 30 JA=1,NP
       DO 30 KA=1,NP
         A(JA) = A(JA) + Z(KA)*P(JA,KA)
30    CONTINUE
     CS = 0.0D+0
     DO 40 JC=1,NP
       CS = CS + Z(JC)*(B(JC)-BS(JC))
       CG(JC) = CG(JC) + Z(JC)*RISD/SIG2(I)
40    CONTINUE
     C = Y(I) - CS - ETA
     DO 50 IB=1,NP
       B(IB) = B(IB) + (A(IB)*C)/DELTA
50   CONTINUE
     DO 41 ISV=1,NP
       DO 41 JSV=1,NP
         PSV(JSV,ISV) = P(JSV,ISV)
41    CONTINUE
    DO 52 IV=1,NP
       DO 52 IU=IV,NP
         SUMP = 0.0D+0
         DO 51 KP=1,NP
           DO 51 JP=1,NP
             IF(KP-IV.EQ.0.OR.JP-IU.EQ.0) GOTO 51
             PSQ1 = PSV(KP,JP)*PSV(IU,IV)
             PSQ2 = PSV(IU,KP)*PSV(IV,JP)
             PSQ = PSQ1 - PSQ2
         IF(DABS(PSQ1)+DABS(PSQ2).LT.1.D-15) THEN
           RP = PSQ * 1.D15
           ELSE
             RP = PSQ / (DABS(PSQ1)+DABS(PSQ2))
         END IF
             RP = ABS(RP)
             RPP = RP - 1.0D-12
             IF(RPP.LE.0.0D+0) THEN
               PSQ = 0.0D+0
             END IF
             SUMP = SUMP + Z(JP)*Z(KP)*PSQ
51        CONTINUE
         P(IU,IV) = (PSV(IU,IV)*SIG2(I)+SUMP)/DELTA
52    CONTINUE
     DO 53 IV=2,NP
       IVM = IV - 1
       DO 53 IU = 1,IVM
         P(IU,IV)= P(IV,IU)
53    CONTINUE
     IF(IPRINT.GT.0) THEN
       IF(I.EQ.1) THEN
     WRITE(7,*)
     WRITE(7,*)'SEQUENTIAL ESTIMATES OF THE PARAMETERS GIVEN BELOW'
        WRITE(7,'(//,3X,"I",6X,"ETA",5X,"RESIDUALS",7X,
   1"B(1)",8X,"B(2)",8X,"B(3)",8X,"B(4)")')
```

```
   EN
    W
   EN
100 CO
C--EN
C--ST
C
C   ST
   IF(
103 SS
   IF(
105 D
    B
210 C
   W
212 F
   G
104 
   D
   B
102
   A
   A
110
   
116






113

314

114
C
115





112

10
```

```
          END IF
          WRITE(7,'(I4,6E12.5)')I,ETA,RISD,(B(JC),JC=1,NP)
        END IF
100   CONTINUE
C --- END BASIC LOOP, GIVES B(I) AND SY
C --- START BOX-KANEMASU MODIFICATION
C
C     START BOX-KANEMASU MODIFICATION
      IF(MAX-1)104,104,103
103   SS=SY/2.0D+0
      IF(SS-SYP)104,104,105
105   DO 210 IBS=1,NP
       B(IBS)= BSV(IBS)
210   CONTINUE
      WRITE(IOUT,212)
212   FORMAT(7X,'USE BSV(IBS)')
      GOTO 211
104   CONTINUE
      DO 102 IBS=1,NP
      BSS(IBS)= BS(IBS)
102   CONTINUE
      ALPHA= 2.0D+0
      AA= 1.1D+0
110   ALPHA= ALPHA/2.0D+0
      DO 116 IBS=1,NP
       BS(IBS)= BSS(IBS) + ALPHA*( B(IBS)-BSS(IBS) )
       BSV(IBS)= BS(IBS)
116   CONTINUE
      INDEX=0
      G= 0.0D+0
      DO 115 IP=1,NP
       DELB= BS(IP)-BSS(IP)
       G= G + DELB*CG(IP)
       RATIO= DELB/( BSS(IP)+EPS )
       RATIO= ABS(RATIO)
       IF(RATIO-EPSS)113,113,114
113     INDEX= INDEX+1
       WRITE(IOUT,314)
314     FORMAT(7X,'MAX',8X,'NP',5X,'INDEX',8X,'IP')
       WRITE(7,'(7I10)') MAX,NP,INDEX,IP
114     CONTINUE
C     WRITE(7,122) I,Y(I),ETA,RISD,Z(IP),XYP,DELB,SIG2(I)
115   CONTINUE
      SYP= 0.0D+0
      DO 117 I3=1,N
       I=I3
       CALL MODEL
       RISD= Y(I)-ETA
       SYP= SYP + RISD*RISD/SIG2(I)
117   CONTINUE
      IF(NP-INDEX)106,106,107
106   H=1.0D+0
```

GC
107 C
SY
IF
111 I
109 V
108 I
1'
W
1001
1002
I

1003

112

130

131

132

118
211

121

12

C

20
20

13

13

```
      GOTO 132
107   CONTINUE
      SYN= SYP*0.999D+0
      IF(SYN-SY)112,112,111
111   IF(ALPHA-0.01D+0)109,109,110
109   WRITE(7,108) ALPHA,SYP,SY
108   FORMAT(3X,'ALPHA TOO SMALL,ALPHA=',F12.6,2X,'SYP=',E15.6,2X,
     1'SY',E15.6)
      WRITE(7,1001)
1001  FORMAT(8X,'Z(1)',10X,'Z(2)',10X,'Z(3)',10X,'Z(4)',10X,'Z(5)')
1002  FORMAT(6E13.4)
      DO 1003 J=1,N
        CALL SENS
        WRITE(7,1002) (Z(I),I=1,NP)
1003    CONTINUE
      GOTO 1000
112   CONTINUE
      SKSUM= SY - ALPHA*G*( 2.0D+0-1.0D+0/AA )
      IF(SYP-SKSUM)131,131,130
130   H= ALPHA * ALPHA*G/( SYP-SY+2.0D+0*ALPHA*G )
      GOTO 132
131   CONTINUE
      H= ALPHA*AA
132   CONTINUE
      DO 118 IBN= 1,NP
        B(IBN)= BSS(IBN) + H * ( B(IBN)-BSS(IBN) )
118   CONTINUE
211   CONTINUE
      WRITE(IOUT,121)
      WRITE(*,121)
121   FORMAT(5X,'MAX',10X,'H',13X,'G',12X,
     1'SY',11X,'SYP')
      WRITE(7,122) MAX,H,G,SY,SYP
      WRITE(*,122) MAX,H,G,SY,SYP
122   FORMAT(I8,1F13.6,4E14.6)
      WRITE(7,'(10X,"B(",I1,") = ",F16.6)') (I,B(I),I=1,NP)
      WRITE(*,'(10X,"B(",I1,") = ",F16.6)') (I,B(I),I=1,NP)
C     END       BOX-KANEMASU MODIFICATION
      WRITE(7,'(/,5X,"P(1,KP)",9X,"P(2,KP)",9X,"P(3,KP)",9X,
     1"P(4,KP)",9X,"P(5,KP)")')
      DO 206 IP=1,NP
        WRITE(7,207) (P(IP,KP),KP=1,NP)
206   CONTINUE
207   FORMAT(5D15.7)
      WRITE(7,135)
135   FORMAT(5X,'CORRELATION MATRIX')
      DO 136 IR=1,NP
        DO 136 IR2=1,IR
          AR= P(IR,IR) * P(IR2,IR2)
          R(IR,IR2)= P(IR,IR2)/SQRT(AR)
136   CONTINUE
      DO 137 IR=1,NP
```

137
I
C

126

220

127

119

12

12

1

1

1
C
1

C
C
C
C
C
C
C
C
C
C
C
C
C
C

```
      WRITE(7,'(5E15.7)') (R(IR,III),III=1,IR)
137   CONTINUE
      DO 126 IPS=1,NP
C       PS(IPS,IPS)= (1.0E+7) * P(IPS,IPS)
        PS(IPS,IPS)= BS(IPS)*BS(IPS)*10.0D+0
126   CONTINUE
      WRITE(7,*)'XTX(I,K),K=1,NP'
      DO 220 K=1,NP
220   WRITE(7,'(5E15.7)')(XTX(K,III),III=1,NP)
      WRITE(7,*)'XTY(I),I=1,NP'
      WRITE(7,'(5E15.7)')(XTY(I),I=1,NP)
127   FORMAT(3X,'IPS=',I4,3X,'PS(IPS,IPS)=',D15.8)
      DO 119 IP=1,NP
        XTY(IP)=0.0D+0
        DO 119 KP=1,NP
          P(IP,KP)= PS(IP,KP)
          XTX(IP,KP)=0.0D+0
119   CONTINUE
      DO 120 IP=1,NP
        BS(IP)= B(IP)
        CG(IP)= 0.0D+0
120   CONTINUE
      WRITE(7,314)
      WRITE(7,'(7I10,4F10.4)') MAX,NP,INDEX,IP
      IF(NP-INDEX)101,101,123
123   CONTINUE
      M=ITMAX
      IF(MAX-M)99,99,101
101   CONTINUE
      IF(IPRINT)133,133,134
133   IPRINT=IPRINT+1
      GOTO 99
134   CONTINUE
C
1000  CONTINUE
      CLOSE(IIN)
      CLOSE(IOUT)
C                                                 C
C*************************************************************C
C                                                 C
CECCCCCCCC          ERROR MESSAGES                     BLOCK 0900
C                                                 C
C                                                 C
C*************************************************************C
C                                                 C
CFCCCCCCCC          FORMAT STATEMENTS                  BLOCK 9000
C                                                 C
C                                                 C
C*************************************************************C
C
      STOP
      END
```

2. S

C

C
C
C
C
C
C
C

C
2

2. Subroutine For The Estimation Of K_1 And K_2 For Model 1:

```
      SUBROUTINE MODEL
C     THIS SUBROUTINE IS FOR CALCULATING ETA, THE MODEL VALUE
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION  T(1000,5),Y(1000),SIG2(1000),B(5),Z(5),
     +A(5),BS(5),VINV(5,5),EXTRA(20)
      DIMENSION P(5,5),PS(5,5)
      COMMON T,Z,BS,I,ETA,PS,P,B,A,Y,SIG2,MODL,VINV,NP
     +,EXTRA
      COMMON/MOD/AA,TL
C     WRITTEN BY JAMES V. BECK
C     MODL=1 FOR C1
C     MODL=2 FOR C2
C     MODL=3 FOR C1 AND C2
C
C
C      MODEL 1, FOR ONE PARAMETER IN THE CHEMICAL REACTION MODEL, C1
      IF(MODL .EQ. 2)GOTO 200
      IF(MODL .EQ. 3)GOTO 300
      BET1=BS(1)
      BET2=EXTRA(1)
       EXX=EXP(-T(I,1)*(BET1+BET2))
       ETA=BET1*(1.0D+0-EXX)/(BET2*EXX+BET1)
      GOTO 1000
C     MODEL 2, FOR CHEMICAL REACTION, ONE PARAMETER, C2
 200  CONTINUE
       BET1=EXTRA(1)
       BET2=BS(1)
       EXX=EXP(-T(I,1)*(BET1+BET2))
       ETA=BET1*(1.0D+0-EXX)/(BET2*EXX+BET1)
       GOTO 1000
C     MODEL 3, FOR CHEM. REACTION, TWO PARAMETERS, C1 AND C2
 300   CONTINUE
       BET1=BS(1)
       BET2=BS(2)
       EXX=EXP(-T(I,1)*(BET1+BET2))
       ETA=BET1*(1.0D+0-EXX)/(BET2*EXX+BET1)
1000   CONTINUE
       RETURN
       END
C
C
```

3. Sensitivity Coefficient Subroutine:

```
      SUBROUTINE SENS
C      THIS SUBROUTINE IS FOR CALCULATING THE SENSITIVITY COEFFICIENTS
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION T(1000,5),Y(1000),SIG2(1000),B(5),
     +Z(5),A(5),BS(5),VINV(5,5),EXTRA(20)
      DIMENSION P(5,5),PS(5,5)
      COMMON T,Z,BS,I,ETA,PS,P,B,A,Y,SIG2,MODL,VINV,NP
     +,EXTRA
      COMMON/MOD/AA,TL
       DELTA=1.000001D+0
       CALL MODEL
C
      IF(MODL .EQ. 2)GOTO 200
      IF(MODL .EQ. 3)GOTO 300
C
C      MODEL 1, FOR C1
       BET1=BS(1)*DELTA
       BET2=EXTRA(1)
       EXX=EXP(-T(I,1)*(BET1+BET2))
       ET=BET1*(1.0D+0-EXX)/(BET2*EXX+BET1)
       Z(1)=(ET-ETA)/((DELTA-1.0D+0)*BS(1))
       GOTO 1000
C       MODEL 2, FOR C2
200     CONTINUE
       BET1=EXTRA(1)
       BET2=BS(1)*DELTA
       EXX=EXP(-T(I,1)*(BET1+BET2))
       ET=BET1*(1.0D+0-EXX)/(BET2*EXX+BET1)
       Z(1)=(ET-ETA)/((DELTA-1.0D+0)*BS(1))
       GOTO 1000
C       MODEL 3, FOR C1 AND C2
300     CONTINUE
       DO 150 JJ=1,NP
       IF(JJ .EQ. 1)BET1=BS(1)*DELTA
       IF(JJ .EQ. 1)BET2=BS(2)
       IF(JJ .EQ. 2)BET1=BS(1)
       IF(JJ .EQ. 2)BET2=BS(2)*DELTA
       EXX=EXP(-T(I,1)*(BET1+BET2))
       ET=BET1*(1.0D+0-EXX)/(BET2*EXX+BET1)
       Z(JJ)=(ET-ETA)/((DELTA-1.0D+0)*BS(JJ))
 150   CONTINUE
      WRITE(7,*)I, Z(1)*BS(1), Z(2)*BS(1)
1000     CONTINUE
      RETURN
      END
```

4. Sample Input:

```
    20  2  2  50  3  1
    0.01  0.01
 1   0.000000E+00      1.000000       71.000000      130.000000
 2   3.378000E-03      1.000000       79.000000      130.000000
 3   3.378000E-02      1.000000      150.000000      130.000000
 4   3.209000E-02      1.000000      159.000000      130.000000
 5   8.953000E-02      1.000000      230.000000      130.000000
 6   8.784000E-02      1.000000      238.000000      130.000000
 7   1.622000E-01      1.000000      302.000000      130.000000
 8   1.571000E-01      1.000000      309.000000      130.000000
 9   1.655000E-01      1.000000      317.000000      130.000000
10   2.365000E-01      1.000000      380.000000      130.000000
11   2.331000E-01      1.000000      387.000000      130.000000
12   2.534000E-01      1.000000      395.000000      130.000000
13   3.142000E-01      1.000000      460.000000      130.000000
14   3.142000E-01      1.000000      367.000000      130.000000
15   3.953000E-01      1.000000      530.000000      130.000000
16   3.834000E-01      1.000000      538.000000      130.000000
17   3.970000E-01      1.000000      545.000000      130.000000
18   4.628000E-01      1.000000      609.000000      130.000000
19   4.510000E-01      1.000000      617.000000      130.000000
20   4.696000E-01      1.000000      624.000000      130.000000
  0
```

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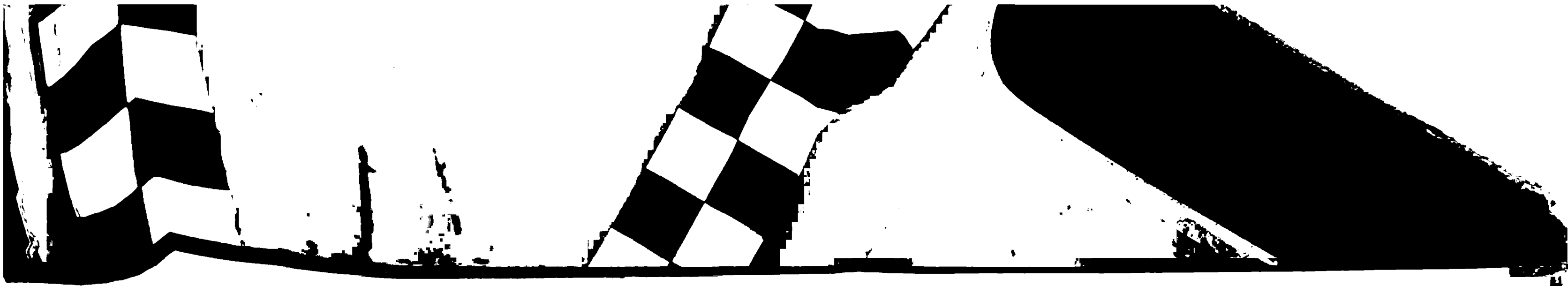

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