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DIELECTRIC MONITORING AND CONTROL OF AN AUTOMATED RESIN TRANSFER MOLDING PROCESS

A Thesis

Presented to the Department of Chemistry

The College of William and Mary in Virginia

In Partial Fulfillment

of the requirements for the Degree of

Master of Arts

---

by

Philip John Kingsley

December 1991

APPROVAL SHEET

This thesis is submitted in partial fulfillment of the
requirements for the degree of

MASTER OF ARTS

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Approved, December 1991

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Abstract

This investigation explores frequency-dependent electromagnetic sensing (FDEMS) as a method of gathering in-situ data and monitoring the curing of an epoxy resin. Ultimately, FDEMS is used to form a closed-loop cure control system for the fabrication of a composite part by Resin Transfer Molding.

Chapter I explores the chemistry of epoxy resins and discusses the resin used in this investigation, British Petroleum E905L.

Chapter II discusses the theory and practical side of the instrumentation used gather data for this paper.

Chapter III discusses composite materials and describes the RTM process developed during the course of this inquiry.

Chapter IV describes the correlation of two physical quantities with dielectric output.

Chapter V details the controlling computer code and describes an actual RTM run.

INTRODUCTION

In this investigation, frequency-dependent electromagnetic sensing (FDEMS), differential scanning calorimetry (DSC) and rheological techniques are to be used to characterize the experimental British Petroleum epoxy resin, E905L. The characterization will include a correlation between degree of cure (alpha), viscosity (η) and the dielectric loss, scaled to frequency (e"*w), where w $=2\pi$ * frequency.

This knowledge of E905L and its curing kinetics will be employed in the design of a closed-loop, intelligent cure controlling system for the fabrication of graphite/E905L composite parts by the Resin Transfer Molding (RTM) process. FDEMS will serve to close the automation loop of such a system.

Through its ability to take in-situ data, FDEMS will monitor the molecular state of the resin during the fabrication of a part. Software will use this data to decide the time/temperature scheme that will most efficiently ensure complete wet-out of the fiber preform and then bring the part to the desired degree of cure.

CHAPTER I
EPOXY RESINS

The polymeric resin system studied in this investigation was British Petroleum E905L Epoxy Resin. Thus, a general introduction to the widely varied class of compounds known as epoxy resins is needed.

An epoxy resin can be defined as a group of oligomeric molecules containing one or more epoxy groups[1]. (fig 1-1). The epoxy ring is both polar and strained, making it a highly reactive group.

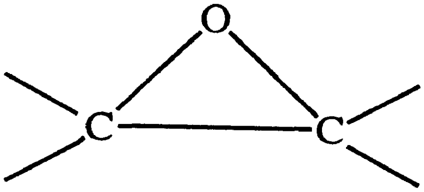


fig. 1-1 epoxy group

The first commercially available epoxy resins appeared in 1946. Since then their use has grown steadily and in 1987, 332 MMlbs of epoxy resin were sold in the United States[2]. Approximately half of this amount was used for coatings while the other half was used for structural applications, such as laminates and composites.

Epoxy resins have many desirable properties. They possess good thermal stability, excellent adhesiveness to many materials, good electrical properties and low shrinkage upon cure[3]. Uncured resin properties, such as viscosity and reaction temperature, and final part properties, including heat resistance and flexibility, can be tailored to suit the user by modification of the monomeric structure(s). Often, these advantages justify the comparatively higher cost of epoxy resins.

Chemistry of Epoxy Resins

In 1987, 94% of all epoxy resin sold was based on the difunctional molecule, the diglycidyl ether of bisphenol A (DGEBPA) (fig.1-2)[4].

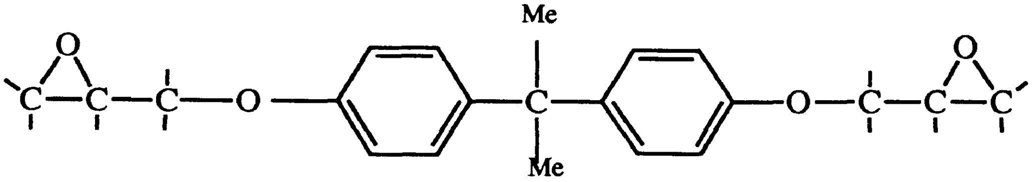
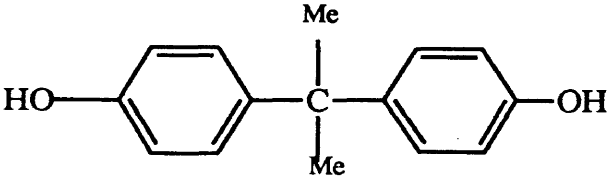
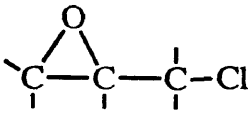


fig. 1-2 DGEBPA

i. Synthesis of DGEBPA: DGEBPA is synthesized by reacting bisphenol A with epichlorohydrin (fig. 1-3).



bisphenol A



epichlorohydrin

fig. 1-3

NaOH catalyzes the first step of this reaction, the nucleophilic cleavage of the epichlorohydrin epoxy by the bisphenol hydroxyl group[5]. This gives the following dichlorohydrin intermediate (fig. 1-4).

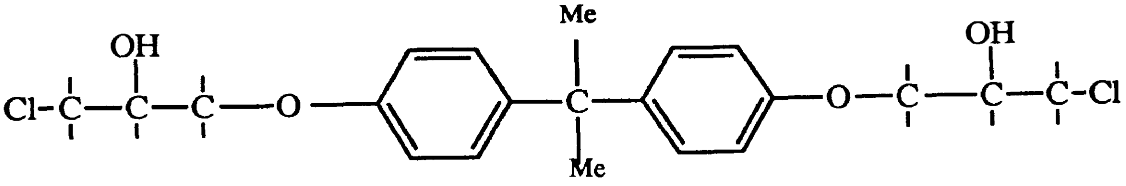


fig. 4-1

This intermediate then undergoes dehydrohalogenation to generate DGEBPA. The dehydrohalogenation is carried out with a stoichiometric amount of NaOH[6]. In industry, the two above reactions occur simultaneously. A possible consequence of this is the production of resin epoxies before all the bisphenol A molecules are consumed. Thus, resin epoxies are sometimes attacked instead of the epichlorohydrin epoxies, which leads to (fig. 1-5).

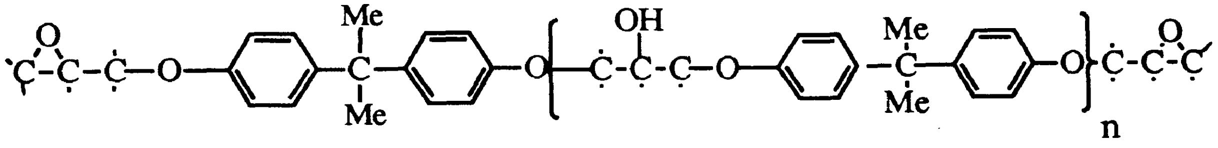


fig. 1-5

Properties of the uncured resin vary with n, thus n is modified to meet user demands. For example, low values of n give low-viscosity resins, which are desirable for structural or composite use. The n value is controlled by the mole ratio of epichlorohydrin to bisphenol A. A mole ratio of 10:1 gives monomeric DGEBPA (n=0)and as the mole ratio decreases, n and viscosity increase.

ii. Curing Reactions: Cure is the term used to describe the reaction which transforms a low molecular weight polymeric resin into a highly cross-linked solid network. Epoxy resins always contain one, often several, coreactants; substances that effect the cure. Coreactants are either catalytic or serve as comonomers.

a. Catalytic Coreactants: A catalytic coreactant is present in very small quantities and either initiates epoxy homopolymerization or accelerates the cure process with some comonomer. Epoxy resin catalysts are usually Lewis bases, Lewis acids or sometimes photoinitiators. Below is an example of how a Lewis acid catalyst initiates epoxy homopolymerization.

While many Lewis acid catalysts are possible, commercially, the most important is boron triflouride (BF_3). BF_3 causes rapid epoxy cure, and often dangerous exotherms, at room temperature. Because of this, BF_3 is usually complexed with monoethylamine to give [BF_3 $NH_2C_2H_5$] (BF_3MEA). The catalytic effect of BF_3MEA at room temperature is negligible, it requires a temperature range of 80-100 C to initiate a curing reaction. The BF_3MEA-catalyzed homopolymerization of DGEBPA proceeds in the following manner The epoxy groups solvate the catalyst, creating an oxonium ion[7] (fig. 1-6).

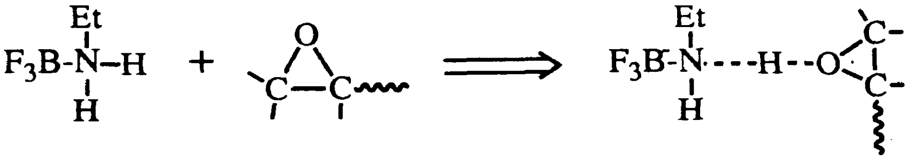


fig. 1-6

which is then attacked by other epoxy groups (fig. 1-7).

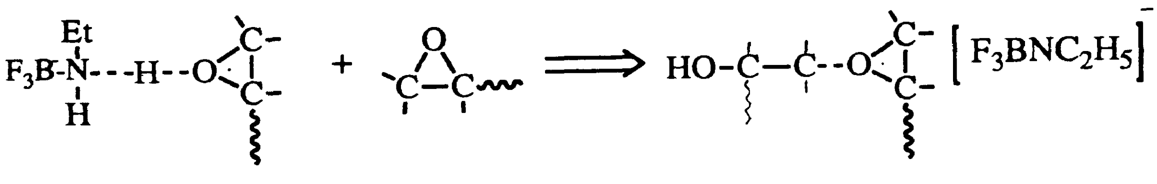


fig. 1-7

This process continues until a highly crosslinked network is formed (fig. 1-8).

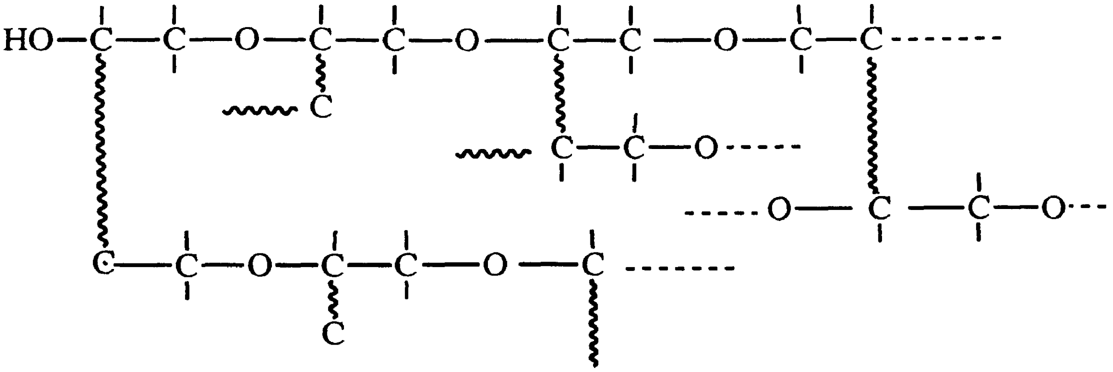


fig. 1-8

b. Copolymeric coreactants: Numerous materials are used as comonomers with epoxy resins. Amines, acid anhydrides, formaldehyde resins and many other classes of chemicals have been used as comonomers in epoxy cure. This wide range of choices provides the user with a wide range of neat (or uncured) and cured properties. Amines are very common curing agents. The curing mechanism of a primary amine/DGEBPA system is described below (fig. 1-9).

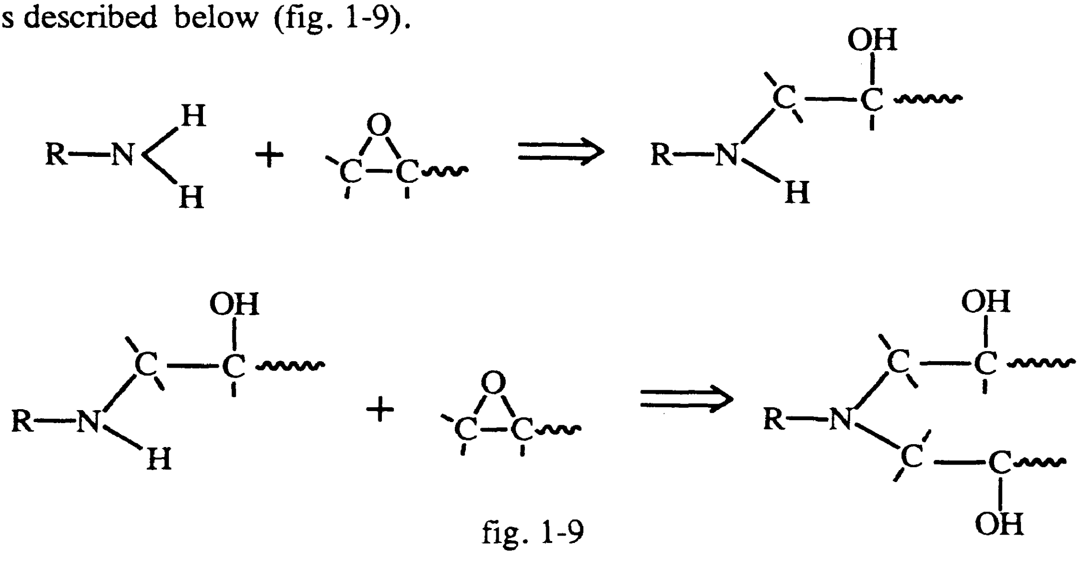


fig. 1-9

We see in figure 1-9 that each amine hydrogen opens an epoxy ring. For this to occur, an active hydrogen compound such as water or an alcohol must be present in at least impurity levels[3]. The hydroxyl groups produced as a result of the ring cleavage serve to further react with other epoxy groups (fig. 1-10).

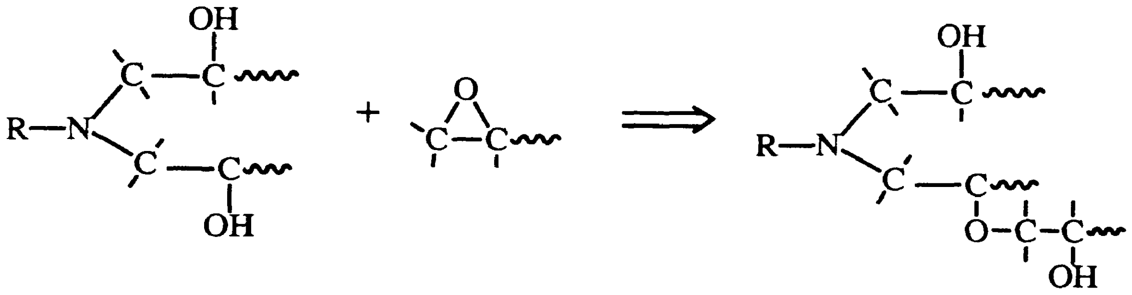


fig. 1-10

This process continues, amine H's and hydroxyl groups reacting with epoxies, until a very complex three-dimensional network results (fig. 1-11).

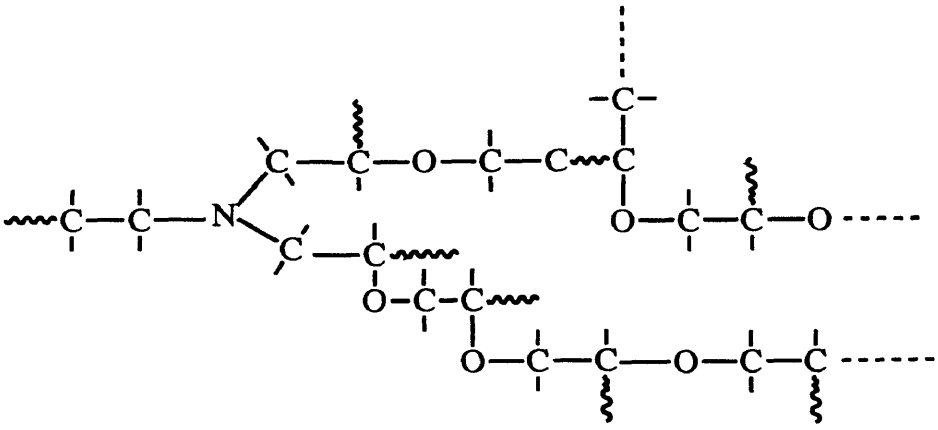


fig. 1-11

iii. Molecular Structure and Resin Properties: The characteristics of both cured and uncured resin are greatly effected by the molecular structure of the resin. This section will briefly discuss some aspects of this relationship.

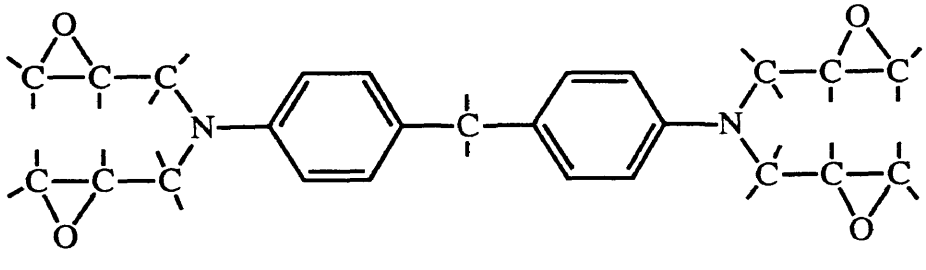
a. Aliphatic groups: Aliphatic groups between the functionalities of the epoxy or the curing agent tend to lower the viscosity of the uncured resin. The presence of a hydrocarbon chain with few constituents reduces the possible intramolecular attractions such as hydrogen bonding. Aliphatic chains also reduce the chance of "entanglement" with adjacent molecules compared to a highly substituted molecule. These factors allow resin molecules to slide past one another with relative ease.

Aliphatic amine curing agents generally provide a lower temperature cure than their aromatic counterparts, often at room temperature, due to their increased nucleophilicity[9]. Consequently, resin systems with aliphatic amines tend to have comparatively short working lives once the epoxy and curing agent have been mixed.

Systems cured with aliphatic-containing monomers have a higher degree of flexibility, due to the unhindered rotation of aliphatic chains. This, however, causes these resins to be more susceptible to thermal degradation.

b. Aromatic groups: Aromatic constituents in either component of an epoxy system tend to effect the resin in a manner opposite to the aliphatic groups. Bulky aromatic groups increase room temperature viscosity. Their relatively smaller nucleophilic character, in the form of amines, increases their required cure temperature. In a cured part, aromatic rings are resistant to thermooxidative attack and are often incorporated into resins intended for high-temperature uses[10]. Aromatic rings also increase the rigidity of the cured part.

c. High Performance Resins: Aromatic rings and multifunctionality characterize a class of epoxy resins known as high-performance epoxy resins. The maximum glass transition temperature (T_g) of DGEBPA systems is approximately 180-190 C[11], and most of these systems have T_g's in the range of 130-150 C. This is insufficient for many aerospace applications. Since T_g is proportional to the crosslink density, high performance resins are designed to achieve a higher degree of crosslinking by employing polyfunctional monomers. The standard high performance resin system is composed of the epoxy tetraglycidylmethylenedianiline (TGMDA) and the curing agent diaminodiphenylsulfone(DDS) (fig. 1-12).



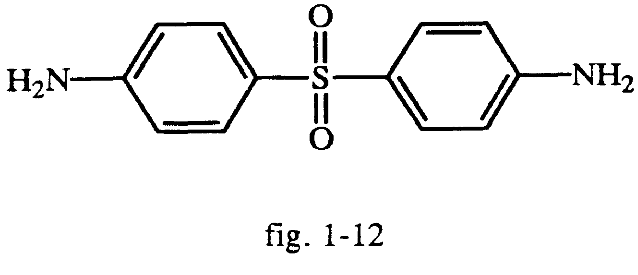


fig. 1-12

The curing reactions are the same as described previously and the tetrafunctionality of both components increases the crosslink density of the cured resin, producing a T_g in the range of 250 C[12]. Additionally, the aromatic rings increase the rigidity of the final product.

BP E905L Epoxy Resin

Since the early 1980's researchers have been trying to improve upon the qualities of high performance resins for use in increasingly demanding aerospace and outer space applications. The resin employed in this investigation, BP E905L, is one such resin and being an experimental resin, information about it is limited.

The E905L resin system is a 50/50 weight% mixture of 2 components. Component A is a 70/30 weight% mixture of medium and low molecular weight triazine resins,[13] respectively. A triazine resin is composed of monomers or oligomers with the cyanate group (fig. 1-13) on an aromatic ring[14].

$$-O-C\equiv N$$

fig. 1-13

The dicyanate structure is the general form of monomeric triazine resin (fig. 1-14).

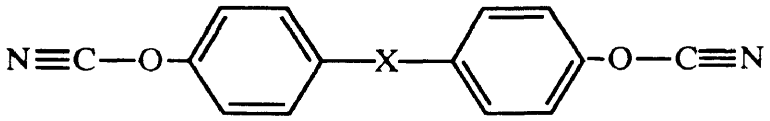


fig. 1-14

However, upon heating the dicyanate undergoes a cyclotrimerization reaction resulting in a trisubstituted aromatic triazine ring (fig. 1-15)[15].

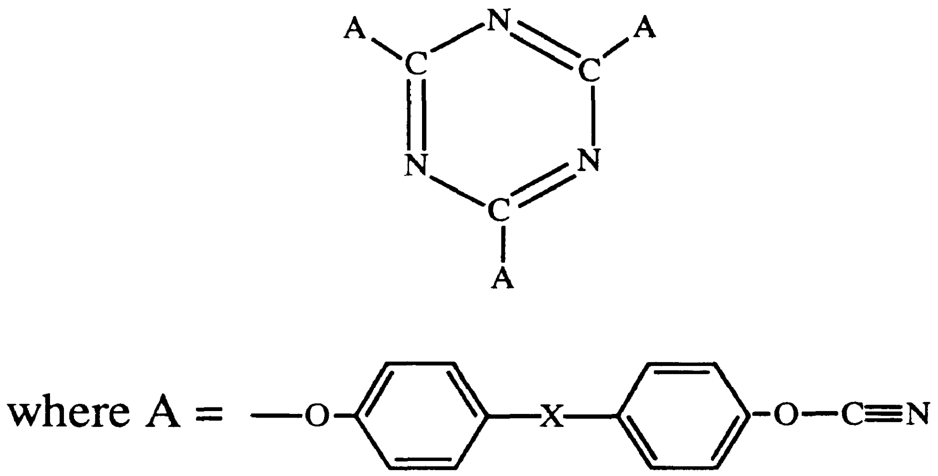


fig. 1-15

Further heating causes the -O-C-N groups to participate in other triazine rings, eventually leading to a crosslinked solid. However, this process can be halted and stable oligomers can be recovered as liquids or semi-solids[16]. Thus low and medium molecular weight triazine resins exist as limited networks of the trisubstituted triazine ring system shown in fig. 1-15.

Component B is a three species mixture. The main ingredient, 75 +/-10% by weight, is the diglycidyl ether of bisphenol F (fig. 1-16)[17].

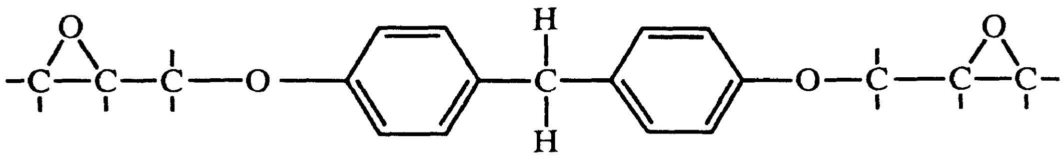


fig. 1-16

The second component, 25 +/-10% by weight, is an amine-epoxy toughening agent[18]. Since this is an experimental resin, the exact structure is unavailable but fig. 1-17 is an artist's conception of a possible amine-epoxy toughening agent.

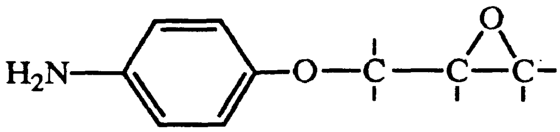


fig. 1-17

Finally, an organometallic catalyst, of which there are hundreds, is present at less than 1% by weight[19].

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CHAPTER II
INSTRUMENTATION

Frequency-dependent electromagnetic sensing (FDEMS), differential scanning calorimetry and rheometry were the primary experimental techniques employed in this investigation. Thus an explanation of the basic theory of each is in order.

I. FDEMS

The electrical properties of most polymers can be studied with a capacitor. This is due to the fact that most polymers and their monomers are dielectrics, or insulating materials. In this investigation, the resin of interest fills a capacitor and its electrical properties are monitored by the use of alternating electric fields throughout the course of the resin's curing reaction.

Polarization and Polarizability

A polar molecule, although electrically neutral, has regions of localized positive and negative charge due to the electrical properties of its component atoms.

Polarization can be induced in non-polar molecules in an electric field. The total polarization of such a molecule is the sum of three components. One is known as dipole polarization. This is the orientation of a permanent dipole in an electric field. The second is electronic polarization; this results from the shifting of electron clouds of a molecule in response to an electric field. The third is atomic polarization, which is due to the shifting of the nuclei of the molecule's atoms. Figure 2-1 illustrates these three phenomena.

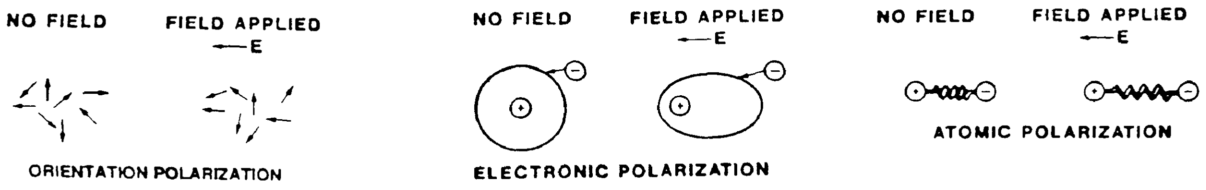


fig. 2-1

Polarization can be represented as:

$$P = P_o + P_e + P_a \qquad (2\text{-}1)$$

where the subscripts o, e and a represent dipole, electric and atomic polarization respectively.

These three polarization mechanisms are reflected in the physical quantity called polarizability[1]. An electric field, E, is applied to a piece of matter resulting in the net field E'. E' varies from the applied field due to the polarization of the medium. E' induces an average polarized dipole moment, m, that is proportional to itself.

$$m = a_T * E' \qquad (2\text{-}2)$$

α_T, the proportionality constant, is the polarizability. It has units of C^2mN^{-1} (coulomb^2 meter/newton) and can be represented in the additive form:

$$\alpha_T = \alpha_o + \alpha_e + \alpha_a \qquad (2\text{-}3)$$

where o, e and a retain their original meanings.

The total polarized dipole moment for a given volume with n molecules or repeat units, is m*n, which is equal to the polarized charge density, P. This is the general expression for polarization[2]:

$$P = m * n = a_T * E' * n \qquad (2\text{-}4)$$

Capacitance and Permittivity

An ideal parallel plate capacitor is an excellent vehicle to aid understanding of capacitance and permittivity.

Capacitance is defined as the ratio of charge on the plates of a capacitor (q) to the potential difference between them (v). Mathematically:

$$C_o = \frac{q}{v} \qquad (farad = \frac{coulomb}{volt}) \qquad (2\text{-}5)$$

where the subscript o indicates the space between the plates is a vacuum.

When a dielectric is placed between the plates, the capacitance changes. The dielectric material becomes polarized due to the electric field between the plates in a manner illustrated by figure 2-2.

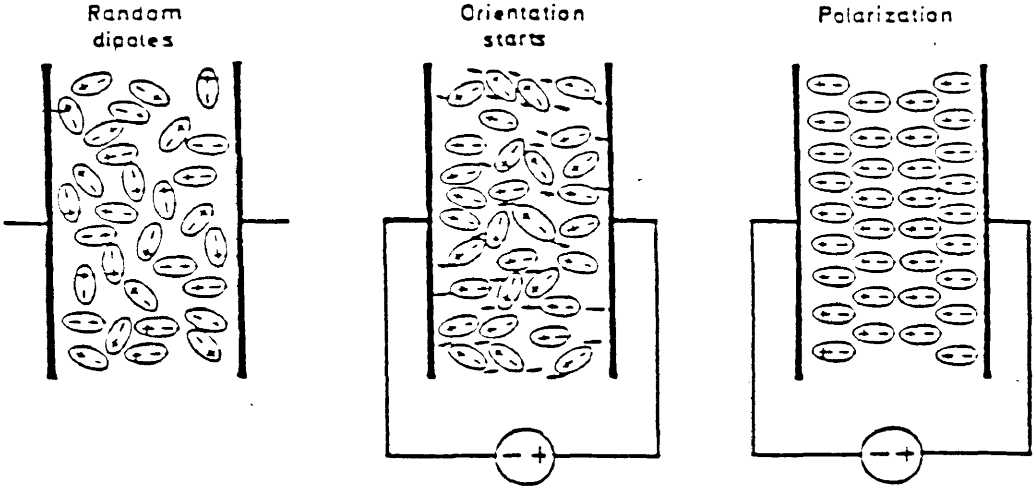


fig. 2-2

Due to this partial alignment, the edges of the dielectric adjacent to the plates now have localized charge (+/-)pand since they are in contact with the plates the charge on the plates becomes (q +p). The capacitance now becomes:

$$C = \frac{(q + p)}{v} \qquad (2\text{-}6)$$

Relative permittivity, e, is defined as the ratio of the capacitance of a capacitor filled with a dielectric to that of one experiencing a vacuum:

$$e = \frac{C}{C_o} \qquad (2\text{-}7)$$

This permittivity is also related to the polarization P produced by the applied field E[3]:

$$e = \frac{1 + 4\pi P}{\epsilon E} \qquad (2\text{-}8)$$

where ϵ is a unit-dependent constant.

Alternating Field Effects on e

When the electrical field between the plates of a capacitor changes sinusoidally, the molecules in this electric field move so as to maintain proper alignment. At low frequencies, the molecules have ample time to reach their equilibrium positions before the field is changed. However, as the frequency of the alternating field increases, the dipolar mechanisms steadily lose their ability to reorient themselves to the new field.

The first mechanism to experience this loss is the orientation or permanent dipole, a_o. The frequency at which a_o drops out ranges from 10^{10-12} Hz for small molecules to 10^2 Hz for polymers.[4]

At frequencies comparable to natural frequencies of vibration of the atoms in a molecule, a_a fails to reach it's equilibrium value. This occurs in the neighborhood of 10^{12-14} Hz. Finally, a_e falls off in the 10^{15} Hz range and beyond[5]. Figure 2-3 illustrates this phenomenon graphically.

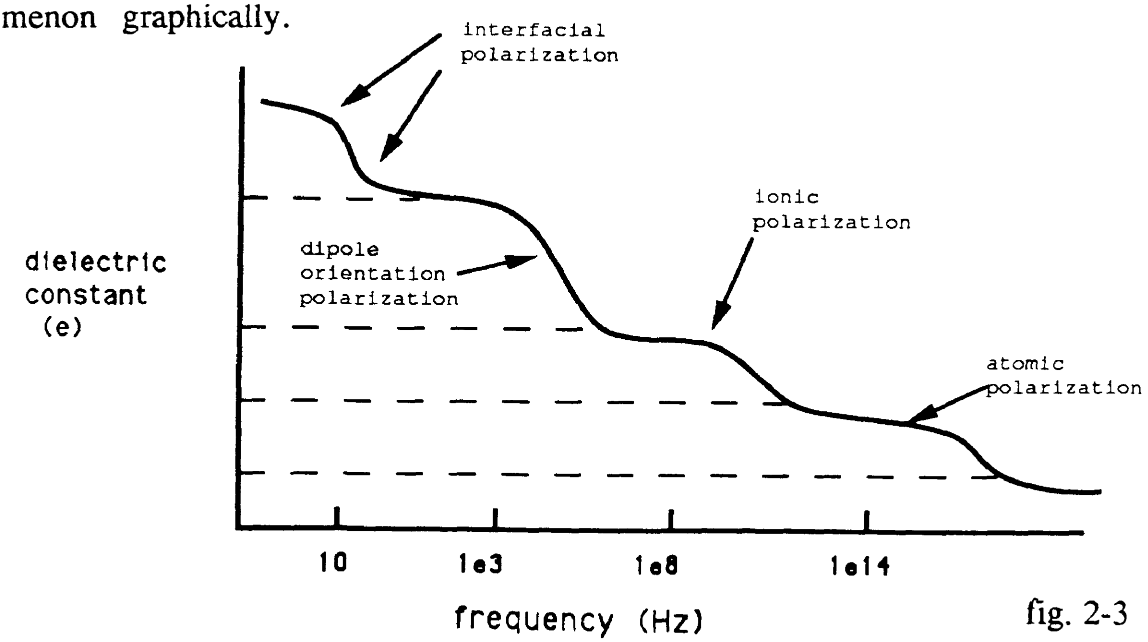


fig. 2-3

Since e $=C/C_o$ and C_o is constant, the drop in e is analogous to dropping capacitance.

e' and e''

The intensive geometry-independent complex permittivity, e^*, is defined as:

$$e^* = e' - ie'' \qquad (2\text{-}9)$$

The real component, e', is the relative permittivity that was discussed above. The imaginary component, e", is also known as the dielectric loss factor. It comes from energy lost due to the time-dependence polarization and ionic conduction.[6]

Using an expression for current, useful expressions for e' and e" may be derived. The current, I, for any circuit composed of a resistor in series with a capacitor that is filled with a dielectric is represented by eqn. 2-10, where V is voltage:[7]

$$I = i2\pi fCV \quad \text{where} \quad C = C_o e^* \qquad (2\text{-}10,11)$$

By substituting 2-9 into 2-11 and then substituting the result into 2-10, we get:

$$I = i2\pi fe'CV + 2\pi fe''C_oV \qquad (2\text{-}12)$$

Ohm's law gives the following expression for the circuit under consideration:[8]

$$Z^{-1} = \frac{I}{V} \qquad (2\text{-}13)$$

where Z is the impedance, or total resistance, of the circuit. A simple substitution of 2-12 into 2-13 produces:

$$Z^{-1} = i2\pi fe'C_o + 2\pi fe''C_o \qquad (2\text{-}14)$$

Impedance is related to the conductance, G, as follows:

$$Z^{-1} = G + i\omega C \qquad (2\text{-}15)$$

Now, setting 2-14 and 2-15 equal, 2-16 is deduced:

$$i2\pi fe'C_0 + 2\pi fe''C_o = G + i2\pi fC \qquad (2\text{-}16)$$

which rearranges to:

$$i2\pi fe'c_o - i2\pi fC + 2\pi fe''C_o - G = 0 \qquad (2\text{-}17)$$

Separating 2-17 into it's real and imaginary components and setting them equal to zero gives:

$$i2\pi fe'C_o - i2\pi fC = 0 \qquad (2\text{-}18)$$

$$2\pi fe''C_o - G = 0 \qquad (2\text{-}19)$$

These become the useful equations:

$$e' = \frac{C}{C_o} \qquad e'' = \frac{G}{2\pi fC_o} \qquad (2\text{-}20,21)$$

e' and e" each have a dipolar and ionic component that can be represented as follows:

$$e^{\prime\prime} = e_d + e_i \qquad\qquad e^{\prime} = e_d + e_i \qquad (2\text{-}22{,}23)$$

The loss factor can also be represented by[9]:

$$e^{\prime\prime} = \frac{(e_{rel} - e_{un})\ \omega\tau}{1 + (\omega\tau)^2} + \frac{\sigma}{\omega e_o} \qquad (2\text{-}24)$$

where e_{rel} =relaxed permittivity, e_{un} =unrelaxed permittivity, $w = 2\pi f$, τ is the dielectric relaxation time, σ is ionic conductivity and e_o is the permittivity of free space. These two terms arise from the dipolar and ionic components of the loss and are represented as such:

$$e_d = \frac{(e_{rel} - e_{un})\ \omega\tau}{(1 + \omega\tau)^2} \qquad\qquad e_i = \frac{\sigma}{\omega e_o} \qquad (2\text{-}25{,}26)$$

These equations can be rearranged to give:

$$e_d\omega = \frac{(e_{rel} - e_{un})\ \omega^2\tau}{(1 + \omega\tau)^2} \qquad (2\text{-}27)$$

$$e_i\omega = \frac{\sigma}{e_o} \qquad (2\text{-}28)$$

This gives us the quantity e"*w and shows that its ionic component is frequency-independent while its dipolar component is not.

Interpretation

At frequencies below 10 Hz, the ionic portion of e" is often dominated by localized layers of charge near the electrodes. These regions of charge give rise to uncharacteristically high e' and e" values[10]. However, a plot of e"*w in the Hz-MHz region can provide much information about a curing resin system. Overlapping e"*w signals, in other words the frequency-independence of the loss term, indicates that ionic translational diffusion is the dominating physical process[11]. As the overlapping frequencies begin to separate, the ionic component no longer is the major factor affecting the loss. Instead, rotational diffusion of bound charge and molecular dipole moments begin to have a greater and greater effect upon e".

Ionic conductivity, σ, is directly proportional to both $e"_i$*w (eqn. 2-28) and ionic mobility. Thus, the drop in e" is paramount to a drop in ionic mobility as the resin goes from a low-viscosity fluid to a high-viscosity crosslinked solid. Finally, as the value of de"/dt approaches zero, the reaction approaches completion.

Experimental

The FDEMS data acquisition system used in this investigation consisted of a Hewlett-Packard 4192A LF Impedance Analyzer controlled by DEKDYNE Data Acquisition software installed on a Zenith 386 Data Systems computer. Conductance and impedance measurements were made in the 50 Hz to 1 MHz range. The raw data was transformed into complex permittivities by the DEKDYNE software.

The capacitors used were disposable, geometry-independent microsensors patented by Kranbuehl. These sensors are comprised of a fine array of interdigitated electrodes on a base of glass or kapton. Kapton-based sensors were most commonly used in this investigation due to their ability to withstand high pressures. The sensors were enclosed in a manner indicated by figure 2-4. This filter system allowed the resin to reach the active face of the sensor while excluding conductive, and thus short-circuiting, graphite fibers.

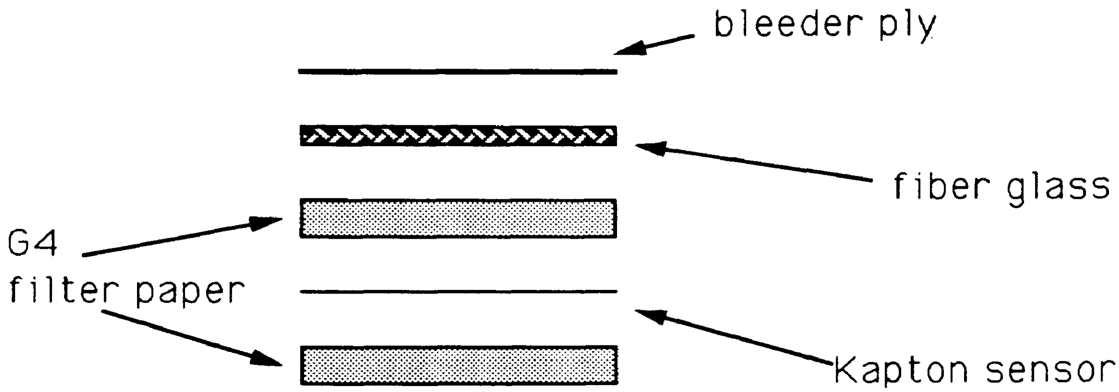


fig. 2-4

II. Differential Scanning Calorimetry

A Differential Scanning Calorimeter is a device that maintains a sample and a reference material at a zero degree temperature difference while the two materials are subjected to the same time-temperature regime and records the energy required to maintain this thermal equilibrium. This technique for measuring thermal properties is called Differential Scanning Calorimetry (DSC). It is a useful tool and provides several pieces of information about a substance such as; glass transition temperature, heating and melting points, heat of reaction and heat capacities.

Two chambers, each with an independent heater and sensor, hold the sample and the reference material (fig. 2-5). A computer applies the desired time-temperature scheme to the chambers and records the data.

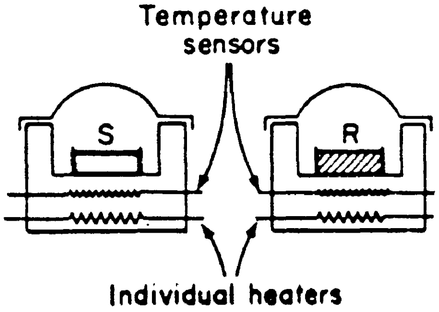


fig. 2-5

Temperature sweeps or ramps and isothermal holds are the two most common types of runs performed on a DSC. Both were used in the course of this investigation. If the monitored process is exothermic, then heat is added to the reference cell and obviously, heat is added to the sample cell should the process be endothermic. A signal proportional to the energy required to maintain thermal equilibrium is recorded against time. The resultant plot of power versus time can be manipulated to give several pieces of information.

A calculation of the some area under the curve gives the enthalpy of the reaction.

$$watt = \frac{joule}{second} \qquad area = watt * time = \frac{joule}{second} * second = joule$$

or mathematically:

$$H_R = \int \frac{dQ}{dt} dt \tag{2-29}$$

where H_R is the enthalpy of reaction and the expression is integrated from 0 to the total run time. Reaction heat in J/g is easily calculated as the sample mass is always known.

Degree of cure, or alpha, is another attainable quantity. Alpha at any time, t, can be calculated:

$$\alpha = \frac{H_t}{H_{rxn}} \tag{2-30}$$

where H_t is the heat at time t and H_{rxn} is the total heat of reaction, which is equal to the heat of an isothermal run plus the heat of its corresponding ramp. $d\alpha/dt$, or rate of reaction, is easily generated once a listing of alphas have been produced for a certain sample. These two quantities provide an excellent picture of the progress of the reaction.

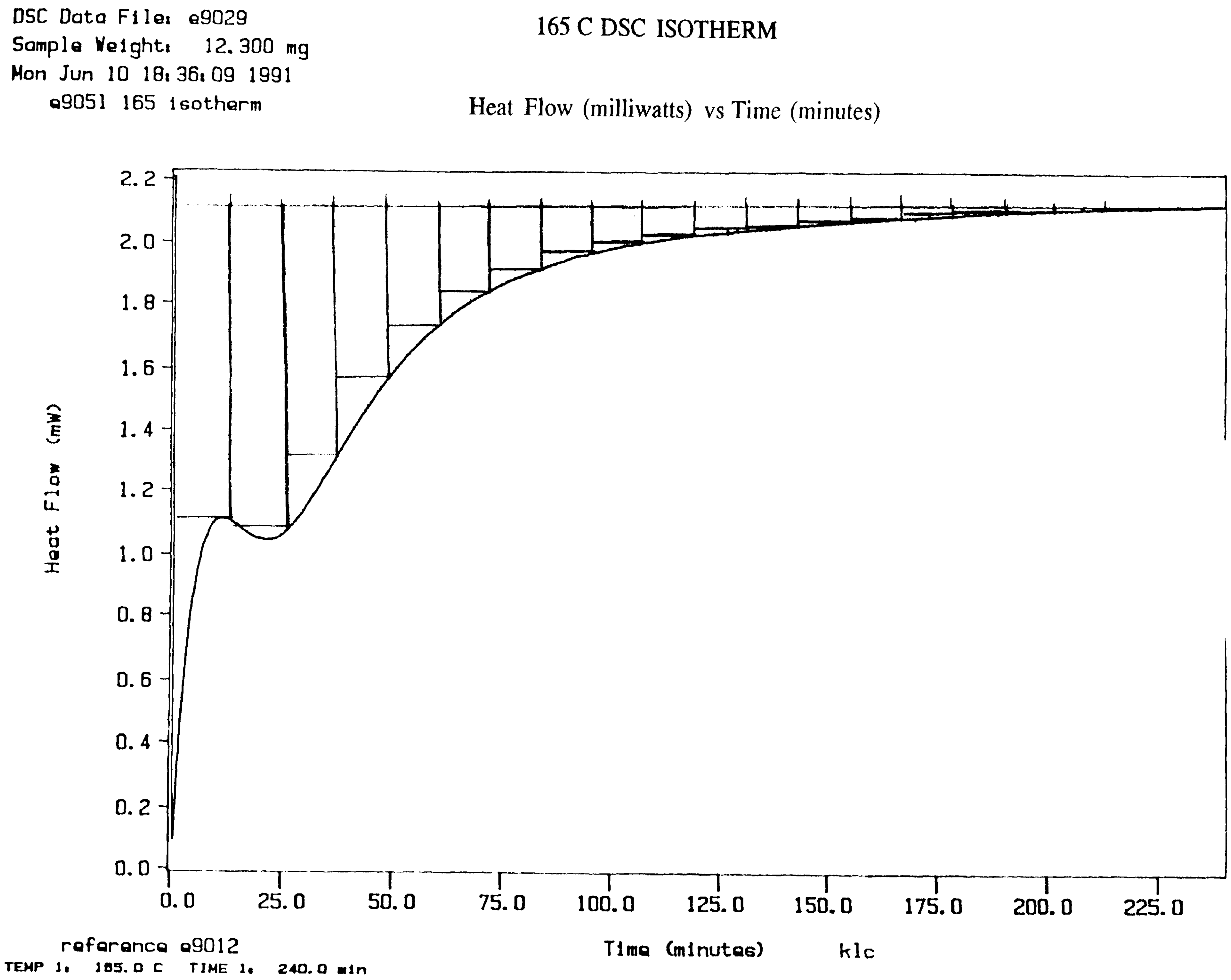
Figure 2-6 is a DSC isotherm of E905L at 165 C and figure 2-7 is its corresponding ramp. In figure 2-6, the area bound by the rectangles indicates the power differential between the sample and reference material. This area is integrated up to 225 minutes, at which point the trace shows a zero rate of change. The result of the integration is the isothermal heat. The rectangles illustrate our integration technique. Of course, the computer generated rectangles are considerably smaller.

The ramp, figure 2-7, is from 50-350 C at a rate of 5 C/minute and it reveals several things. An essentially constant slope exists up to about 160 C, where a slope change indicates a second-order transition. This transition is the partially cured material going through its glass transition temperature, an approximate second-order phase transition. Up to this point, there is no reaction due to the fact that the molecules are locked in position in a glassy solid. Once the T_g is passed, the molecules become much more mobile and are free to react. The levelling and subsequent dropping of the trace indicates an exothermal process, the residual reaction. The reaction slows to a stop around 310 C, where the material begins to thermally degrade slightly.

Experimental

The DSC used is a Perkin-Elmer DSC-7 with a 7500 series Professional Computer. Prior to any DSC run, the sample resin, BP E905L, and reference material, either air or completely cured resin, were sealed in aluminum pans. The sample pan was weighed empty and full so the sample weight could be determined. The pans were then placed in the correct chambers in preparation for the experiment. An isotherm was run at a given temperature until the change in power output was zero. Next, the sample pan was reweighed and ramped from 50 C to 350 C at 5 degrees per minute. This served to completely cure the sample and record its latent (non-isothermal) heat.

Temperature ramps were integrated by TAS7 software on the DSC computer. Isothermal data runs were converted to ASCII files and fed into a computer program written by the author and H. Rhodenizer. The program essentially divided the area to be integrated into many rectangles. It received the residual heat, computed and summed the area of the rectangles, and gave the heat of reaction, alpha and $d\alpha/dt$ for each interval of the isothermal run.



165 C DSC ISOTHERM

Heat Flow (milliwatts) vs Time (minutes)

fig. 2-6

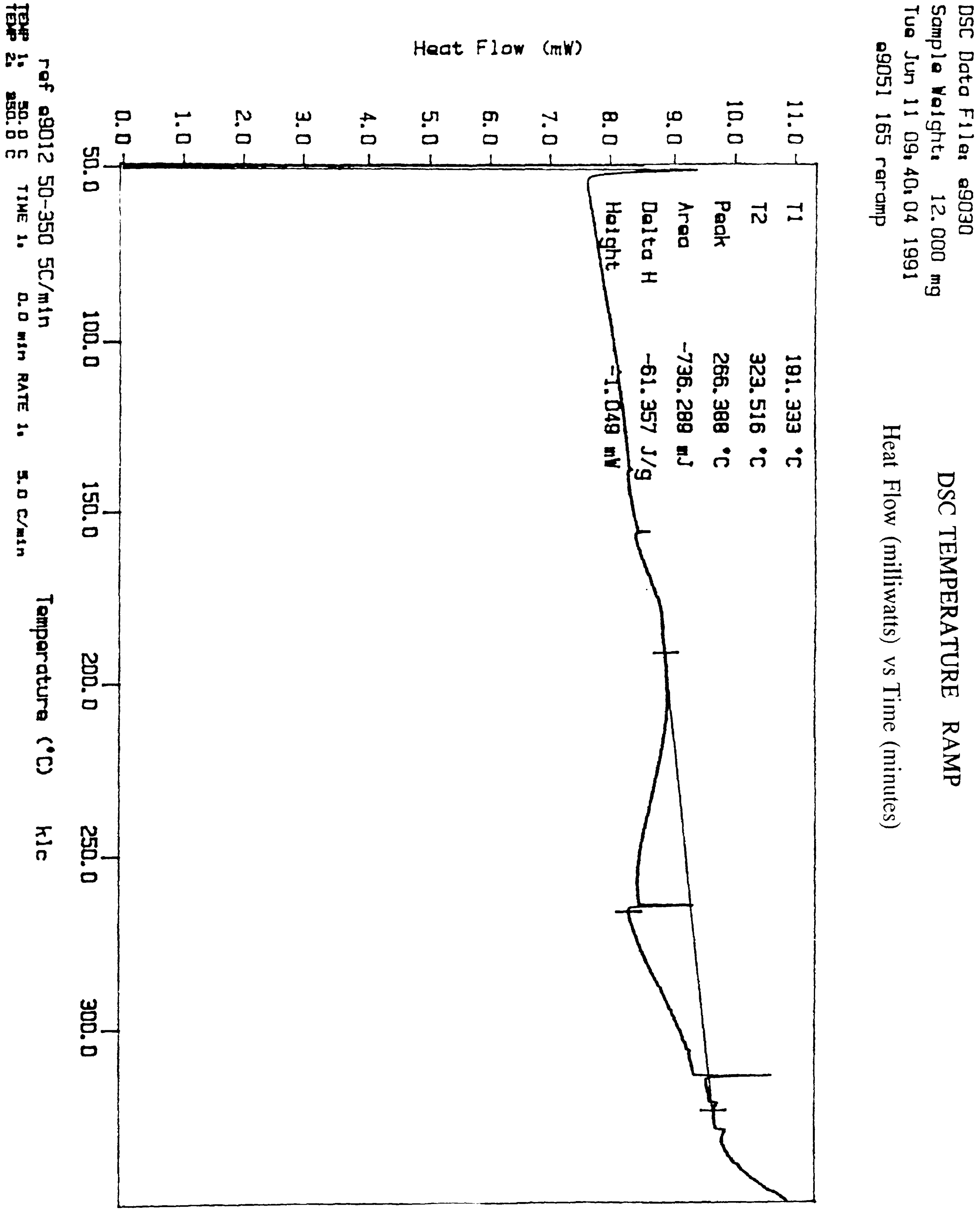

DSC Data File: a9030
Sample Weight: 12.000 mg
Tue Jun 11 09:40:04 1991
a9051 165 reramp
DSC TEMPERATURE RAMP
Heat Flow (milliwatts) vs Time (minutes)
Heat Flow (mW)
T1 181.333 °C
T2 323.516 °C
Peak 266.388 °C
Area -736.289 mJ
Delta H -61.357 J/g
Height -1.048 mW
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
50.0
100.0
150.0
200.0
250.0
300.0
Temperature (°C)
klc
ref a9012 50-350 5C/min
TEMP 1: 50.0 C TIME 1: 0.0 min RATE 1: 5.0 C/min
TEMP 2: 350.0 C

fig. 2-7

III. Rheology

Rheology is the science of the deformation and the flow of matter.[12] Rheological data can provide a great deal of information to the polymer chemist. Molecular weight, molecular weight distribution, glass transition temperature and many other things can be elucidated through rheometry.[13] This investigation is concerned with the viscosity profile and G', G'', gel point relationship of the E905L resin system. Knowledge of these parameters for any resin system is vital to successful processing of that resin system.

Viscosity, or η, is a property that characterizes a fluid's resistance to flow.[14] It is defined as the ratio of stress to rate of strain. Poise(P) and Pascal seconds(Pa.s) are the two common units for viscosity.

$$\eta = 1Pa.s = \frac{N}{m^2}s = 10P$$

As discussed above, viscosity and its relation to time and temperature need to be known. One can get an idea of the viscosity/temperature relationship common to most resin systems by visualizing a substance such as tar. At room temperature, tar may be tacky, almost brittle, and very hard to use. As the temperature increases, the viscosity of the tar decreases and its fluidity increases, making it easier to spread on your roof or driveway.

The difficulty with polymeric resins is that at some point, the temperature will be sufficient to initiate the curing reaction, which increases viscosity. Figure 2-8 is a plot of η versus temperature for BP E905L resin. The temperature profile is a ramp from 60 to

150 at 2 C degrees per minute. Up through temperature of approximately 110 C, the increasing thermal energy serves to disrupt the intermolecular attractions and allow the monomers to slip by one another with increasing ease. The disruptive effect is more significant than the slight crosslinking that is occurring in this temperature range. This is reflected in the dropping viscosity. After this point the heat is sufficiently high to cause the polymerization reaction to proceed at a high rate, which is indicated by the dramatic increase in viscosity. As the resin goes from a mixture of monomers to a highly crosslinked, three-dimensional array, the resin's resistance to flow continually increases until the system is so viscous that the rheometer has difficulty measuring η. At this point however, the resin is beyond processability. Obviously, a state of low viscosity prior to reaction onset is desirable for the RTM injection process.

Chemical gel point is the instant at which the molecular weight of a resin system goes to infinity[15] or the system becomes an infinite network. This property must be known for completing the wet-out process prior to gel is essential for the resin undergoing RTM. The gel point of the viscoelastic E905L resin can be determined rheologically.

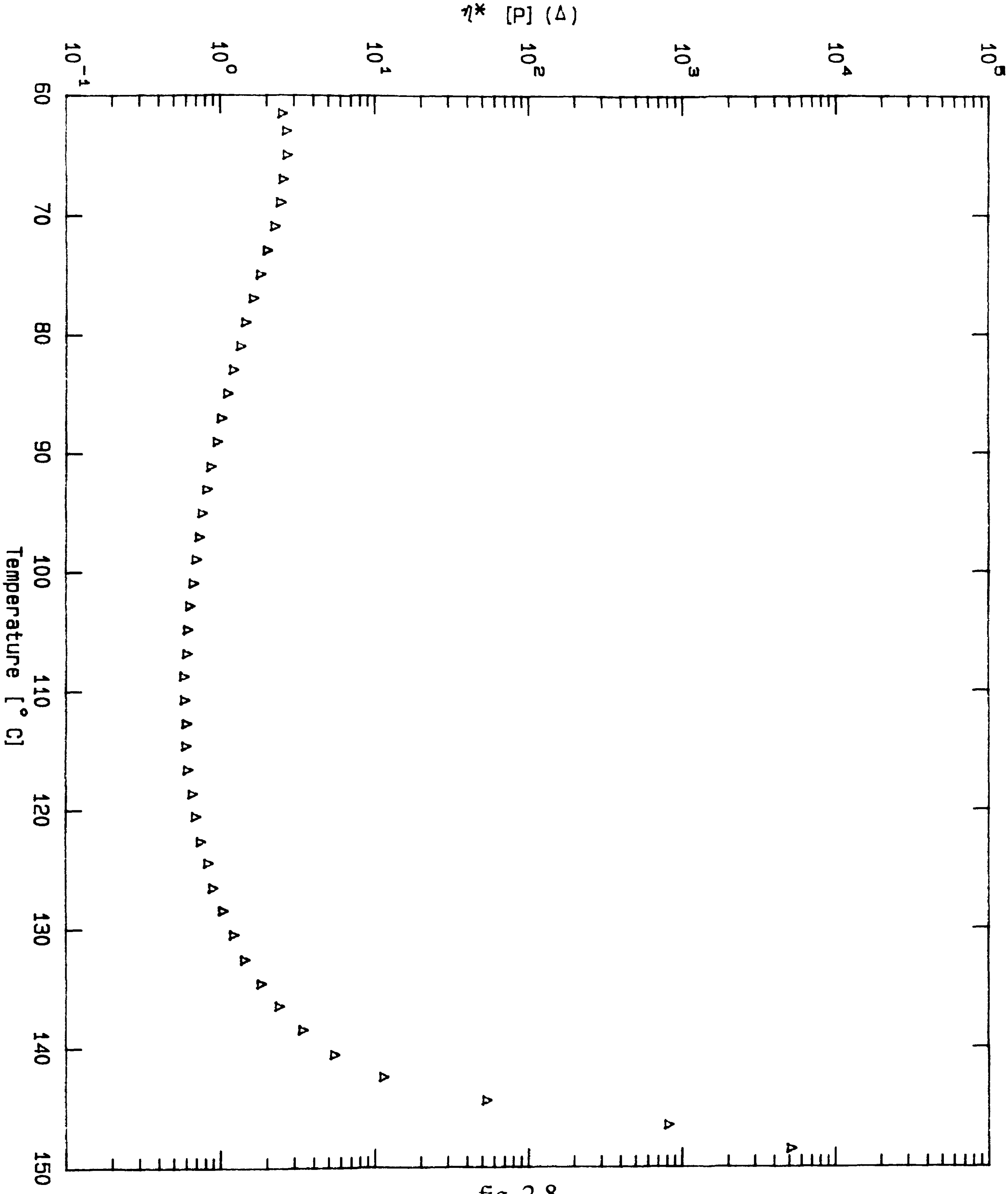
Viscoelasticity means the resin's response to stress is neither completely viscous nor completely elastic but a combination of the two. This is expressed in the material's complex modulus, G^*, which is a measure of the material's overall resistance to deformation. G^* can be written as:

$$G^* = G' + iG'' \qquad (2\text{-}31)$$

G', the elastic storage modulus, is a measure of the material's ability to store deformational energy. G'', the loss modulus, is a measure of the material's ability to dissipate energy as heat. In a resin system such as E905L, equivalent values of G' and G'' indicate the resin's gel point. Figure 2-9 is a plot of G', G'', and temperature against time for E905L. The system gels at approximately 80 minutes, when G' =G''. Note that the viscous component is significantly larger than the elastic component during the first third of the run, in keeping with highly viscous nature of the resin at this point. During the middle third, the two moduli converge and the elastic component becomes the greater quantity. This corresponds to the system changing from a fluid to a solid. The last third of the run sees G' 1-2 orders of magnitude higher than G'', The resin has become a highly crosslinked solid.

Experimental

All rheological experiments were performed on a Rheometrics RDA-700 Dynamic Analyzer, with parallel plate equipment installed. Temperature control, data collection and manipulation were performed by RECAP2 software on a connected IBM PS/2 personal computer. Similar to the DSC experiments, isothermal holds and temperature sweeps were the two types of experiments utilized in this investigation.



Viscosity (P) vs Temperature C

fig. 2-8

G' & G" (dyn/cm^2) vs Time (minutes)

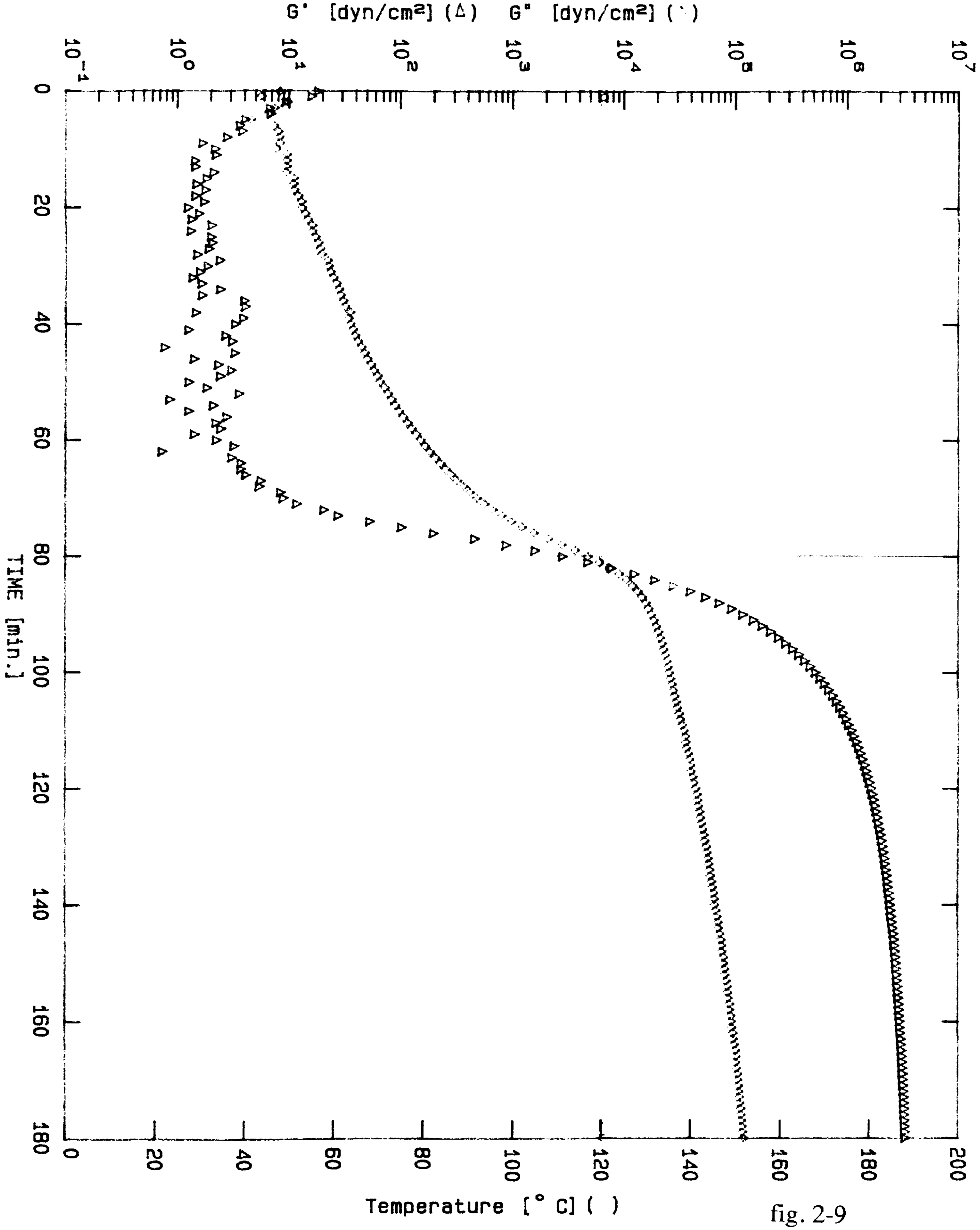


fig. 2-9

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CHAPTER III
COMPOSITE MATERIALS and RTM

Fiber reinforced composite materials, or simply composites, are materials in which fibers are bonded to or embedded in a polymeric resin system[1]. The types of fiber used range from chopped glass to woven carbon or kevlar cloth. The polymeric resin system, or matrix, is most commonly an epoxy or polyester system that will form a 3-dimensional crosslinked network upon curing. However, other materials such as polyimides, nylons and even ceramics also function as matrices. When a matrix is cured around a set of fibers the resultant composite is superior to conventional metal alloys in several ways. It is lighter, has a higher stiffness to weight ratio, is more fatigue and corrosion resistant and has a lower coefficient of thermal expansion[2].

Composites' superiority to metal alloys has led to a great deal of research in this field. A major technological problem is that of fabrication. Composites are not malleable like metal and producing them in large numbers and complex geometries is a difficult and labor-intensive process. Technology that would allow composites to be manufactured on a large scale in any desired shape would be valuable to aerospace, automotive and many other industries.

Current Composite Manufacturing Methods

The following processes are currently commonplace in the composite industry.

i. Spray-up: In spray-up manufacturing, a spray gun is employed to apply the resin matrix and fiber simultaneously to the intended mold. The spray gun takes a roving spool of fiber, usually fiberglass, chops it into short fibers and projects them toward the mold. At the same time, the resin and coreactant are being shot from different nozels and are mixing, along with the chopped fiber, in the air just before the mold surface (fig. 3-1). Once the mold has the proper amount of resin and glass, the mixture is rolled to remove trapped air and thus voids in the parts.

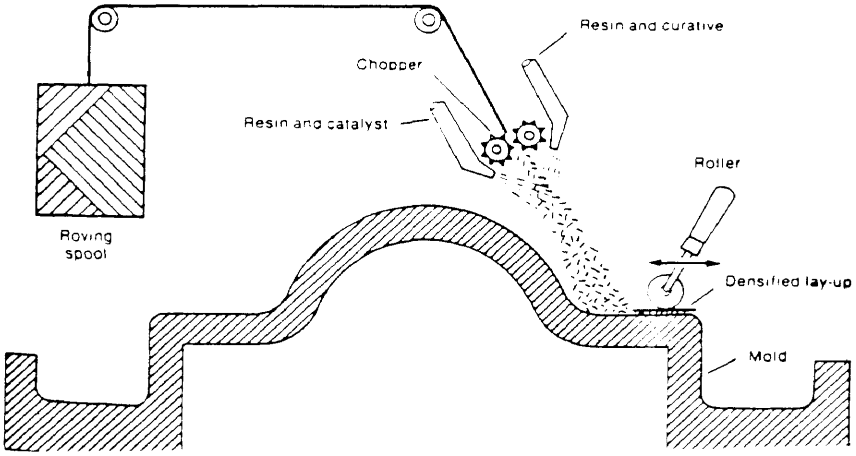


fig. 3-1

Spray-up has the advantages of speed over hand or prepreg lay-up (discussed in the next sections) and the ability to produce complex shapes with relative ease. Spray-up parts are of low fiber-volume fraction and short fiber length, qualities that lead to the disadvantage of relatively weak composite parts. Another disadvantage of the spray-up technique is that operators are exposed to the toxic chemicals of the composite industry.

ii. Hand Lay-Up: In making a composite by hand lay-up techniques, the desired mold is first coated with a release agent and then an initial, thin fiber cloth layer is placed in the mold and saturated with a polyester resin. Subsequent layers of fiber followed by resin coatings are applied on top of the initial layer until the required thickness is achieved. Partial layers are occasionally applied to prevent layers from peeling[3]. Finally, rolling and wiping techniques are used to remove air from the part and prevent voids. The resin used in hand lay-up is generally cured at room temperature but can also be cured in an oven.

iii. Prepregs: A prepreg is a thin sheet of fiber impregnated with a predetermined amount of polymeric matrix[4]. Prepregs are manufactured be first drawing the fibers through a resin bath to saturate them. The wet fibers are then exposed to some sort of heating element which partially cures the resin. Prepregs come in rolls or large sheets and are often used in vacuum and compression molding. Both methods involve cutting the prepregs to the appropriate size and shape and laying them up in the mold. The mold is either compressed or evacuated and is often heated to cure the resin.

These processes are both labor intensive and require a great deal of operator skill, two qualities which are drawbacks to large scale, cheap production. Like spray-up, these processes expose the operator to toxic chemicals.

Advanced Fiber Architecture

The previously discussed manufacturing methods produce parts in which the fibers are discontinuous and randomly oriented, as with spray-up, or are layers of 2-dimensionally woven fabric, like hand lay-up and prepreg. Discontinuous or chopped fiber parts generally have lower strength then a part made from woven fabric[5] and are used in low-performance applications. Although stronger, 2-dimensionally woven parts are subject to the development of cracks in the interply layer.

The interply layer is the layer of resin between two plies of fabric. Cracks in these areas can propagate easily and lead to a separation of the fiber plies, a phenomenon called delamination. Often, this process is the cause of failure in a structure made from composite materials[6]. This interply weakness can be counteracted be adding reinforcing fibers in a third dimension.

3-dimensionally woven fabric preforms are the basis of Advanced Fiber Architecture. Parts made with this type of fabric will be equally as strong as 2-dimensional fabric parts and will resist the weakening effects of delamination. Advanced Fiber Architecture is employed in situations where high-performance is essential. For example, exit and nose cones in rockets and missiles are commonly Advanced Fiber Architecture products.

Resin Transfer Molding

Resin Transfer Molding (or RTM) is a fabrication process that represents an alternative to the labor-intensive, multi-step processes previously described. In RTM, the resin is injected into a closed mold of the desired shape which already contains the correct amount of dry fiber. The mold is then heated to facilitate the curing of the resin. Often, a vacuum is applied to the mold to help remove air, and thus voids, and to draw the resin into the mold. RTM is less labor-intensive than other composite production techniques and once the mold is assembled, it is a one-step process from the individual components to the final part. The closed nature of RTM also lessens the contact between the operator and potentially toxic chemicals.

Because it is a closed mold process where a volume of space is filled with resin, RTM lends itself to the fabrication of high performance parts made with 3-dimensionally woven preforms.

i. RTM at NASA, Langley and William & Mary

While RTM technology has been around for 10-20 years, only recently has it been employed to attempt the fabrication of high-performance parts. Previously, RTM has been used with low-performance, low-viscosity resins to build comparatively weak composite parts. These parts often have a fiber volume fraction of less then 50%. The thrust of this investigation is to use RTM technology to fabricate parts with high-performance, high room temperature viscosity resins at a fiber volume fraction of approximately 60%. The increased fiber volume fraction and increased viscosity greatly reduce the ease with which the resin will flow into the mold and wet out the fiber preform.

All RTM runs described in this paper were preformed at the Langley Research Center in Hampton, VA or at William and Mary in the following manner.

a. Fabric preparation: AS4 12K Locked Stitched graphite cloth is cut with a utility knife to a size slightly smaller than the inside dimensions of the mold. The number of graphite plies varies depending upon the desired thickness of the final part. The number of plies and mass of the preform are recorded.

b. Resin preparation: The previously described BP E905L resin is used. The two components are removed from the freezer and allowed to warm. The desired amount of each component is then transferred to a beaker or quart paint can and allowed to heat to 80 C in order to facilitate mixing. The mass of the components is chosen such that 300-500 grams of a 50/50 weight mixture is produced upon mixing. Once both components have come to temperature, they are thoroughly mixed and then degassed in a vacuum oven preheated to 80 C. The vacuum is applied for at least 15 minutes and held until the resin is needed.

c. Mold Set-Up: The mold itself consists of four aluminum parts: (1) a base plate (2) a border (3) a plunger and (4) a top call plate. The border is a square measuring 7.25" on the outside, 5.75" on the inside and 1 inch high. A semicircular channel is machined into the top and bottom faces of the border. Each channel accommodates a silicon rubber O-ring which serves to form an airtight seal, one with the base plate and one with the top call plate. On opposite sides of the border are two ports that allow resin to enter the mold.

Between the border and base plate lies a silicon rubber gasket and between this gasket and the border lie the sensor leads, either 2 or 3, and two thermocouples. Three slots .008" high and 1" long have been machined in the bottom face of the mold. These slots prevent the leads from rupturing, and thus shorting out against any aluminum surface, when pressure is applied to the mold. The rubber gasket further cushions the leads and thermocouples against rupture and helps from the border/base plate seal.

The plunger is a 5.25" square with a .125" diameter channel running vertically through its center. The channel allows the vacuum to penetrate the fibers and also provides an exit path for excess resin. The thickness of the plunger depends upon the desired thickness of the final part. Either a .75" plunger, giving a .25" thick final part, or a .5" plunger, giving a .5" thick final part, is used.

The top call plate is a square 8" on a side. In its center a .25" diameter channel runs vertically through half the thickness. At the halfway point, the channel makes a right angle and exits the vertical face of the call plate. This channel is the continuation of the vacuum and resin path.

Two ports of the border and the exit port of the top call plate are each fitted with male/male Swagelok joints. The portion of the joint screwed into the aluminum is wrapped with teflon tape to give an airtight seal. A Swagelok nut attaches nylon tubing to the male/male joints. Teflon tape is not necessary at Swagelok nut and screw interfaces. The entire mold assembly is generously treated with mono-coat release agent.

Mono-coat greatly reduces the force required to demold the final part. Figure 3-1 provides a clear(er) view of the mold assembly, which sits in a Carver laboratory press.

d. Injection System: The injection system consists of a vacuum pump, heat/pressure pot, and nylon tubing. The vacuum pump is attached to the exit port of the call plate via a length of nylon tubing, a Swagelok airtight valve and then thick-walled rubber tubing. The valve prevents resin from contaminating the rubber tubing or the vacuum pump.

The pressure pot sits on the floor in front of the press which contains the mold. A step-down joint connects the exit valve of the heat/pressure pot to a male/male Swagelok joint. A length of nylon tubing connects this joint to a T-joint. From the T-joint, two arms of tubing extend to the border injection ports. In order to facilitate resin flow into the mold, the initial arm of tubing is wrapped in heat wrap, as are small portions of the two arms close to the T-joint. Figure 3-2 provides a schematic image of the entire RTM set-up.

e. Typical Injection Conditions:

Heat/pressure pot: The pot contains the degassed resin at a temperature of 65-80 C and a pressure of 16 psig. The pot has a thermostat and pressure regulator which maintain these conditions during the injection process.

Nylon tubing: Since the heating mechanism for the tubing is a wrapping rather than a sheath, maintaining a constant temperature along the tubing is difficult. The temperature directly under the wrapping is often in the 110-115 C range while area between wrap segments is 15-20 C cooler. As a result, the temperature fluctuates sinusoidally along the length of the tubing. The unwrapped portion of the tubing is approximately 30 C, kept slightly above room temperature by conduction from hotter areas of tubing and from the heat given off by the press. Heat wrap is connected to a Variac which keeps the wrap temperature constant during the injection process.

Mold: The mold is under approximately 6500 lbs. of pressure and is maintained in this range throughout the course of the run by hand. Its initial injection temperature is 100 C. Dekdyne data acquisition software regulates the temperature through the Carver press both during and after injection.

ii. Initial RTM Experimentation

RTM experiments were begun in Mid-July at Nasa Langley. The purpose of the initial experiments was to perfect the RTM process and our ability to monitor it dielectrically.

a: Resin Flow Problems: The first RTM run attempted failed to wet-out the sensors. The hardware set-up for this run was similar to that previously described except that heat-wrap was not present on the nylon tubing. When injection began, the resin moved slowly up the tubes and into the mold. As the sensors continued to show no wet-out, the pressure in the heat/pressure pot was increased from 17 to 22 psig. One hour and 45 minutes later, after the sensors remained dry, the run was aborted. Later inspection revealed that a small amount of resin had barely inched into the mold, otherwise there was no resin flow at all.

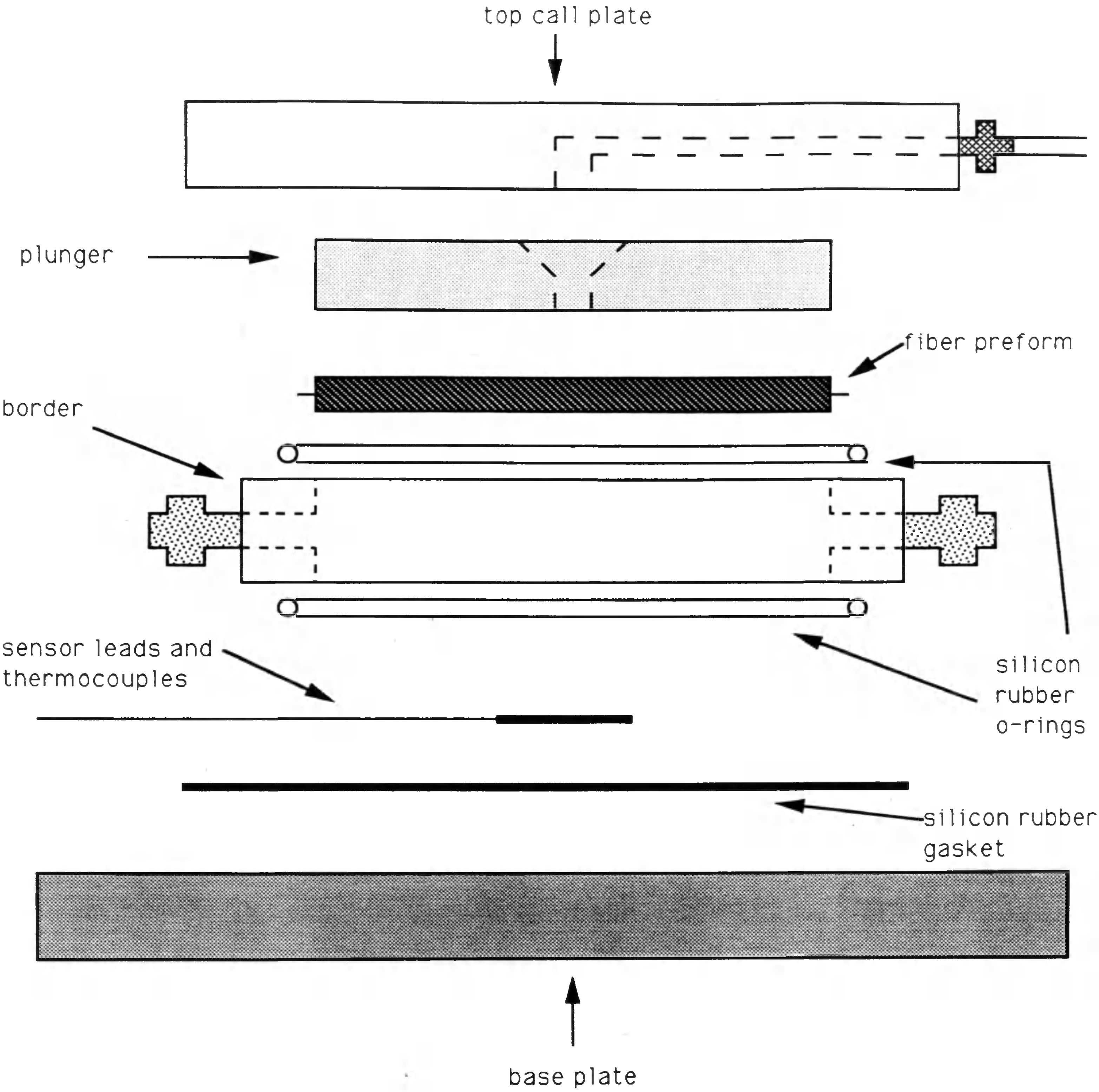
It was theorized that the unheated, uninsulated tubes quickly cooled the resin to room temperature and resin at this temperature is far too viscous to flow through the required tubing. Wrapping heat-wrap along the tubing was suggested as a possible solution and later experimentation confirmed this as a workable plan.

Three 35" lengths of tubing were attached to the heat/pressure pot containing a resin sample. One was naked, the second was insulated with fiberglass tape and the third tube was wrapped in heat wrap. The pot was pressurized to 17 psig for all three runs and both the pot and resin were at 82 C.

The insulated and naked tubes cooled the resin to room temperature prior to the 25" mark along the tube and failed to conduct the resin to the end of the tube within five minutes. The heat-wrapped tube was kept at 61 C while the wrap itself was at 86 C. This length of tubing conducted the resin the 35" in 13 seconds and filled a volume of .5 pints in 2 minutes.

The rate of flow for the heated tubing was acceptable for the RTM process. This experiment showed that a heated resin pathway into the mold is essential for RTM with E905L resin.

b: Sensor Consistency: Inconsistent sensor data due to sensor short-circuiting was another problem initially encountered. Intelligent control of the fabrication process is impossible without consistently accurate sensor readings. Two problems were identified as causing the sensor malfunction. One was that the filter lay-up was to thick and thus, an excess of pressure was being loaded on the sensors. Originally, the filter lay-up was 3 plies thicker than described in Chapter 2. Three layers were removed and the subsequent runs showed no loss in filtering ability. The second problem was that the edge of the mold was cutting through the protective kapton tape of the lead wires. Three 4/1000" high slot approximately 1" wide were machined across the bottom face of the mold to accommodate the leads. This did not prevent lead rupture so an additional 4/1000" was machined off. Again, this did not prevent rupture of the protective kapton. At this point, the silicon rubber gasket between the leads and the bottom plate was employed. Since this innovation, there has been no sensor failure and examinations of the leads have revealed no rupture.

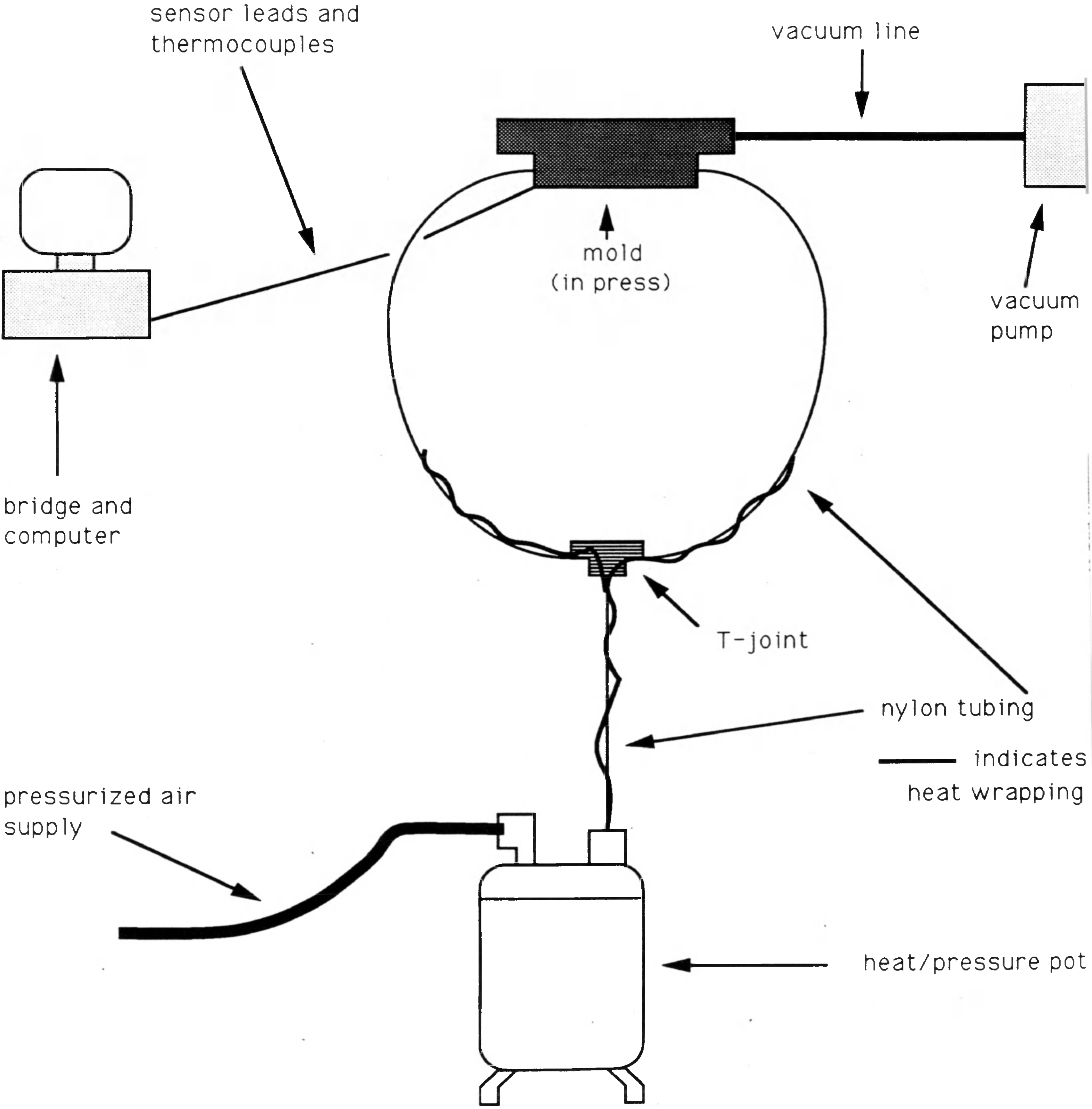


Schematic of Mold Lay-up

fig. 3-1

fig. 3-2

Schematic of Entire RTM System



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CHAPTER IV
CORRELATION of DEGREE of CURE and VISCOSITY

The correlation of α (degree of cure) and η (viscosity) with time, temperature, and the magnitude and frequency-dependence of e^* can be used to produce mathematical models that predict and allow one to monitor the physical state of a resin during an actual run. Such models allow the intelligent design of processing parameters such as injection temperature, lengths of certain isothermal stages of a cure, and run shut-off criteria.

Correlation of η with e"*w

E"*W is correlated with η at temperatures of 80, 100, 110 and 120 C. These temperatures are chosen for use because BP E905L is injected in this temperature range and at higher temperatures rheological data is too limited to permit effective correlation.

Correlation plots are made in the following manner. First, a time(0) is determined for both the rheological and dielectric data. Time(0) for dielectric data is defined as the point when the temperature of the experiment first comes within 4 C of the desired isothermal temperature. Plots of η are often unstable for the first few data points, thus the first "smooth" or congruous point is defined as the rheological time(0).

After time(0)'s have been chosen, eta is then matched with a corresponding e"*w point. In Chapter 2 it was shown that the frequency-independent portion of a typical e"*w vs time plot is proportional to ionic mobility. One goal of this investigation is to track ionic mobility, thus, the ionic or overlapping portion of the dielectric data is used and correlated with viscosity.

The 120 C correlation of viscosity and e"*w will be described for illustrative purposes. Time(0) for the e"*w data (YW813911, fig.4-1) is 13.1 minutes into the actual run, as the temperature at this point has come to 116.5 C. Time(0) for the 120 C viscosity data (e9051 new materials 120 C, fig. 4-2) is actually 5 minutes into the run. A close examination of this plot reveals that points prior to 5 minutes are quite scattered and not consistent with the whole of the experiment, thus they were discarded. Additionally, these first five minutes are necessary for the viscosity to achieve its minimum value and for the resin to achieve thermal equilibrium with the rheometer oven at 120 C.

As previously discussed, η will be correlated with the ionic or overlapping frequencies. 5 kHz was chosen to represent the ionic component of the loss for the first 75 minutes of the run. The two lowest frequencies (50 & 125 Hz) are not joined closely enough to the overlapping band. This is due to the build-up of layers of charge near the electrodes, a phenomenon known as charge polarization. The three highest frequencies (250 & 500 kHz and 1 MHz) are above this band, including 1 MHz, which is off scale. Dipolar effects cause these high signals. Even though the crosslinking in the resin system is very slight at this early stage of cure, these frequencies alternate their respective electric fields too quickly for the molecular dipoles to achieve complete equilibrium with the fields.

Around 75 minutes, the lower frequencies have joined the overlapping, ionic band and

5 kHz has begun to separate. Consequently, the e"*w value was obtained from the 50 Hz signal for the remainder of the points.

Eta is the limiting quantity in this process. The correlation is stopped at 80 minutes because at this time, G' and G" cross, indicating the chemical gel point. Beyond this point, η as a measure of flow is meaningless because the system is crosslinked.

The resultant points of the 120 C correlation were plotted on a log-log scale with e"*w on the y-axis. The plot appears as figure 4-3.

This procedure was also carried out for 110 C, 100 C and for 1 point at 80 C. At 80 C, η is approximately constant for three hours, thus only one e"*w point is needed to dielectrically describe this temperature. A log-log plot of e"*w vs η for all temperatures was generated (fig. 4-4). Note that during the initial stages of the plot, up to η =1e0, the slope of the points is approximately -1. This tells us that viscosity is inversely proportional to e"*w and also ionic mobility. A certain amount of reaction advancement hinders ionic motion approximately as much as it increases resistance to flow.

As the reaction advances, the relationship breaks down and the points start to deviate from the -1 slope. After η =1e0, reaction advancement causes viscosity to increase at a faster rate than ionic mobility is decreasing. The extreme degree of crosslinking at this point of the reaction retards viscous flow much more than it slows ionic migration.

The points were fit to a second degree polynomial (eqn. 4-1) by the SlideWrite program:

$$\log(e''*\omega) = a + b(\log(\eta)) + c(\log(\eta))^2 \qquad (4-1)$$

The values of the coefficients are; a = .1901, b = -.8587 and c = 6.0582. Eta values were obtained by solving the quadratic equation for η.

Alpha Correlation with Time and Temperature

Alpha, or the degree of cure, of a polymer system was defined in Chapter III as the heat at time t divided by the total heat. This section describes how a mathematical model predicting alpha, given the time and temperature history of the resin, was developed.

The DSC ramp (fig. 4-5) of uncured E905L shows two distinct valleys, separated by a peak at 180 C. These two valleys can be thought of as separate exotherms or reactions. Since they occur at two different temperatures, they are known as the low-temp and the high-temp reactions. The total heat at any time is the sum of the individual heats of the two reactions. Producing models for the low and high-temp reactions is necessary to be able to describe the build up of reaction heat and α_{total}. Chiou and Letton describe a method for isolating the separate reactions of a complex-curing epoxy resin. They suggest identifying a temperature at which the reaction rate of one reaction is significantly greater than the rate of the other[1]. This procedure allows one reaction to be aged out, isolating the other reaction, a strategy applied to E905L during this investigation.

The high-temp reaction was modeled in the following manner. First, samples were aged for three hours at 121 C, a temperature at which the low-temp reaction is dominant and goes to completion. Then, data for the high-temp model was obtained by running DSC isotherms of 180, 190, and 215 C, using the aged samples. The integrating program previously described in Chapter II determined the α, $d\alpha/dt$ and heat of reaction values for each of the high-temp reactions; where α ranged from 0 to 1. These values were imported into the fitting program SYSTAT and fit to the nth-order rate law:

$$\frac{d\alpha}{dtime} = k(1 - \alpha)^n \qquad (4\text{-}2)$$

SYSTAT generated k and n values for each temperature. The SYSTAT parameters provided a good fit for the 215 C data, but fits of lesser quality for the other two temperatures. Subsequently, the n value of 215 C, 1.5, was assigned as the n value for 180 and 190 C and their respective k values were estimated. The temperature dependence of these two k's plus the 215 C k was determined with the Arrenhius equation (eqn. 4-3):

$$k = A * e^{-\frac{B}{T}} \qquad \ln k = \ln A - \frac{B}{T} \qquad (4\text{-}3)$$

The natural log of the k's were plotted against their corresponding inverse temperature values (where the temperature is in Kelvin). Then a straight line was drawn through the points. The resultant plot is figure 4-6. The slope of the straight line is -B and its y-intercept is ln A. With these parameters known, the high-temp equation was completed.

The low-temp equation was modeled in a similar manner. Low-temp data was obtained from isothermal runs of 110 and 120 C. However, prior to the SYSTAT modeling, the high-temp equation was used to determine the amount of heat generated by the high-temp reaction during each of the two low-temp isothermal runs. This quantity was subtracted from the low-temp isothermal heat and the difference was fit to equation 4-2 by SYSTAT. The master low-temp equation n was the average of the isothermal n's and the temperature-dependence of k was found via the above graphing method. Thus both high and low-temp k's and n's were elucidated, below are their respective values, where the units of k are min^{-1}.

$$n_{low} = 0.63 \qquad k_{low} = 7.05 \; x \; 10^{9} * e^{-\frac{10443}{T}}$$

$$n_{high} = 1.5 \qquad k_{high} = 1.84 \; x \; 10^{7} * e^{-\frac{9118}{T}}$$

The individual models have been combined in a way that predicts the total α:

$$\alpha_{TOT} = .34 * \alpha(low-temp) + .66 * \alpha(high-temp) \qquad (4-4)$$

As previously mentioned, the α of each temperature-specific model ranges from 0 to 1. These α's must be multiplied by their respective fractions of the total reaction heat before being summed. The low-temp reaction heat, after subtracting out the high-temp contribution, over the total reaction heat is the basis for the coefficient of 0.34. 0.66 is obviously the remainder.

The above fractions of the total heat of reaction do not reflect the areas under the respective low and high-temp curves in figure 4-5. Those areas indicate that 55% +/-4% of the reaction heat is given off from the low-temp reaction. The area-under-the-curve method is misleading, however. It overestimates the low-temp contribution because the area under the low-temp curve contains some high-temp heat while the high-temp area is pure. Thus, high-temp heat is being attributed to the low-temp reaction, making it artificially high while reducing the high-temp heat. The modelling method discussed above corrects for this by back-calculating the high-temp contribution to the low-temp reaction, then modelling the true low-temp heat.

This model provides good agreement with experimental data. Figure 4-7 is a graph of experimental and model-generated α's vs time for 110 and 130 C. For each temperature, the model is represented by a line and the experimental points by markers. As can be seen, the predicted α follows the actual α quite closely. Figure 4-8 is a plot of experimental and model-generated alphas for 150 and 170 C. Again, the line represents the model alpha and the markers depict the experimental degree of cure. The agreement here is not as good as that in figure 4-7, but the model still provides a reasonable picture of the progress of the curing reaction.

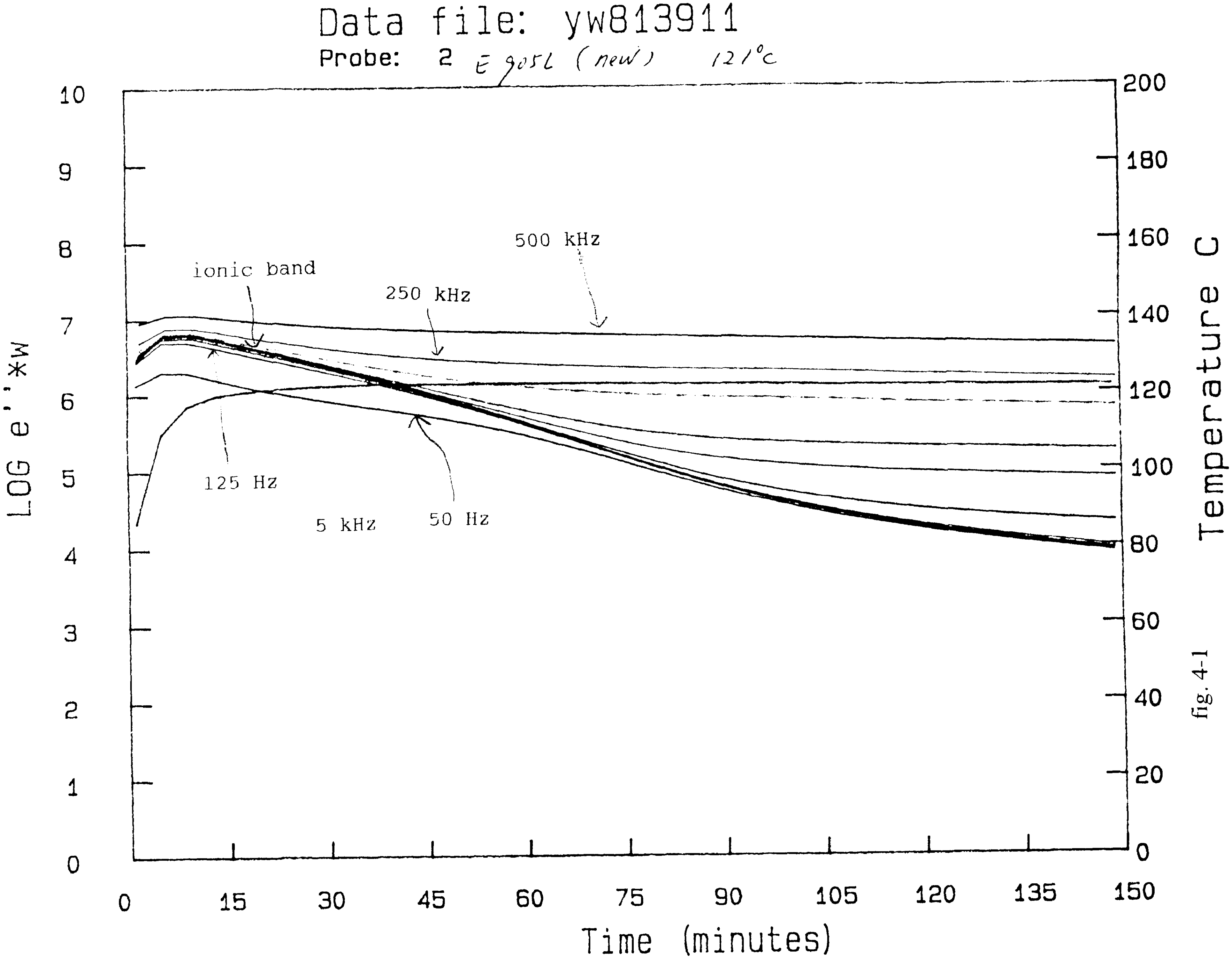
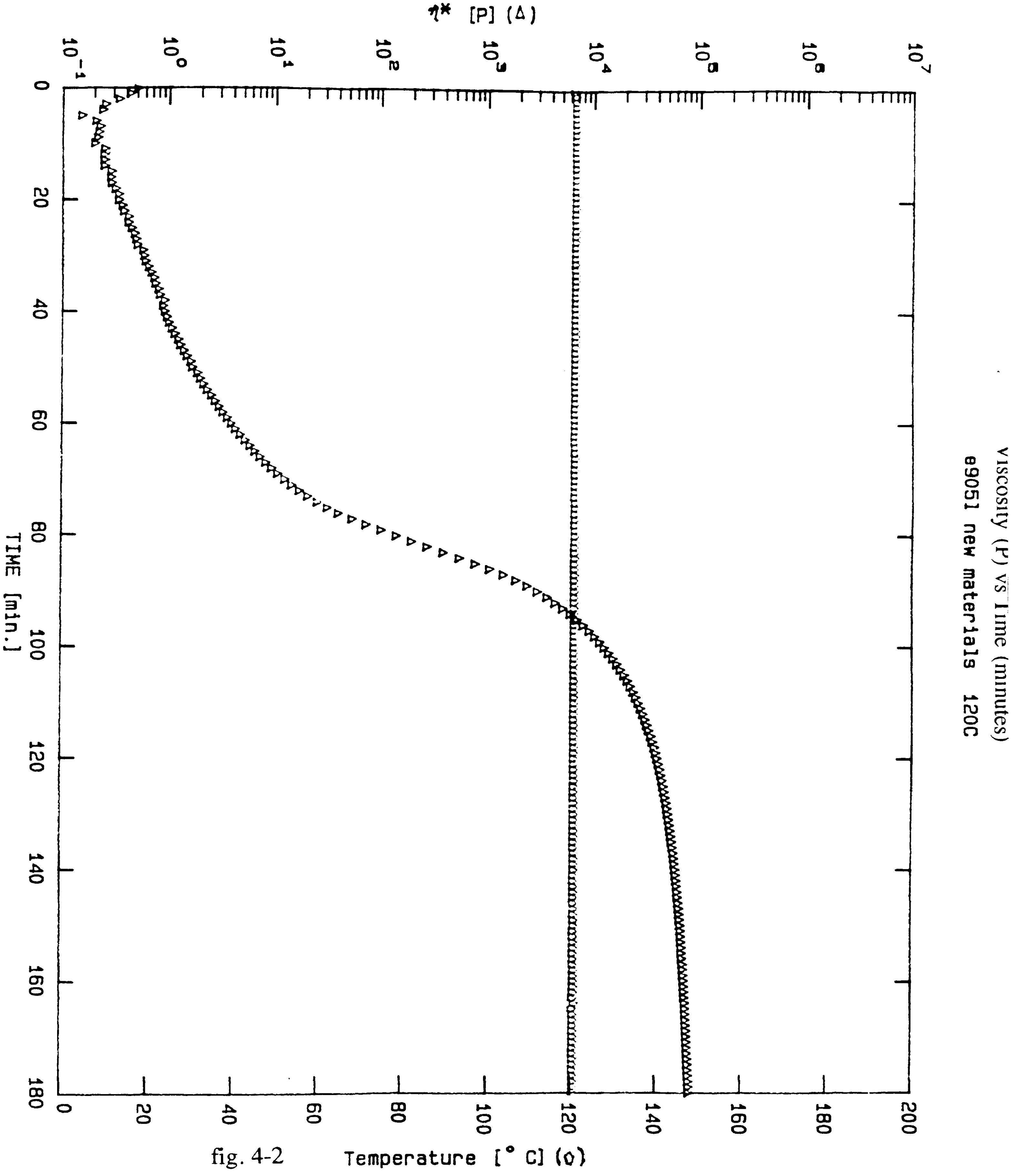

Data file: yw813911
Probe: 2 E 905L (new) 121°C
LOG e''*W
10
9
8
7
6
5
4
3
2
1
0
Temperature C
200
180
160
140
120
100
80
60
40
20
0
Time (minutes)
0
15
30
45
60
75
90
105
120
135
150
500 kHz
ionic band
250 kHz
125 Hz
5 kHz
50 Hz

fig. 4-1



Viscosity (P) vs Time (minutes)
e9051 new materials 120C
η* [P] (Δ)
10⁻¹
10⁰
10¹
10²
10³
10⁴
10⁵
10⁶
10⁷
TIME [min.]
0
20
40
60
80
100
120
140
160
180
Temperature [° C] (◇)
0
20
40
60
80
100
120
140
160
180
200

fig. 4-2

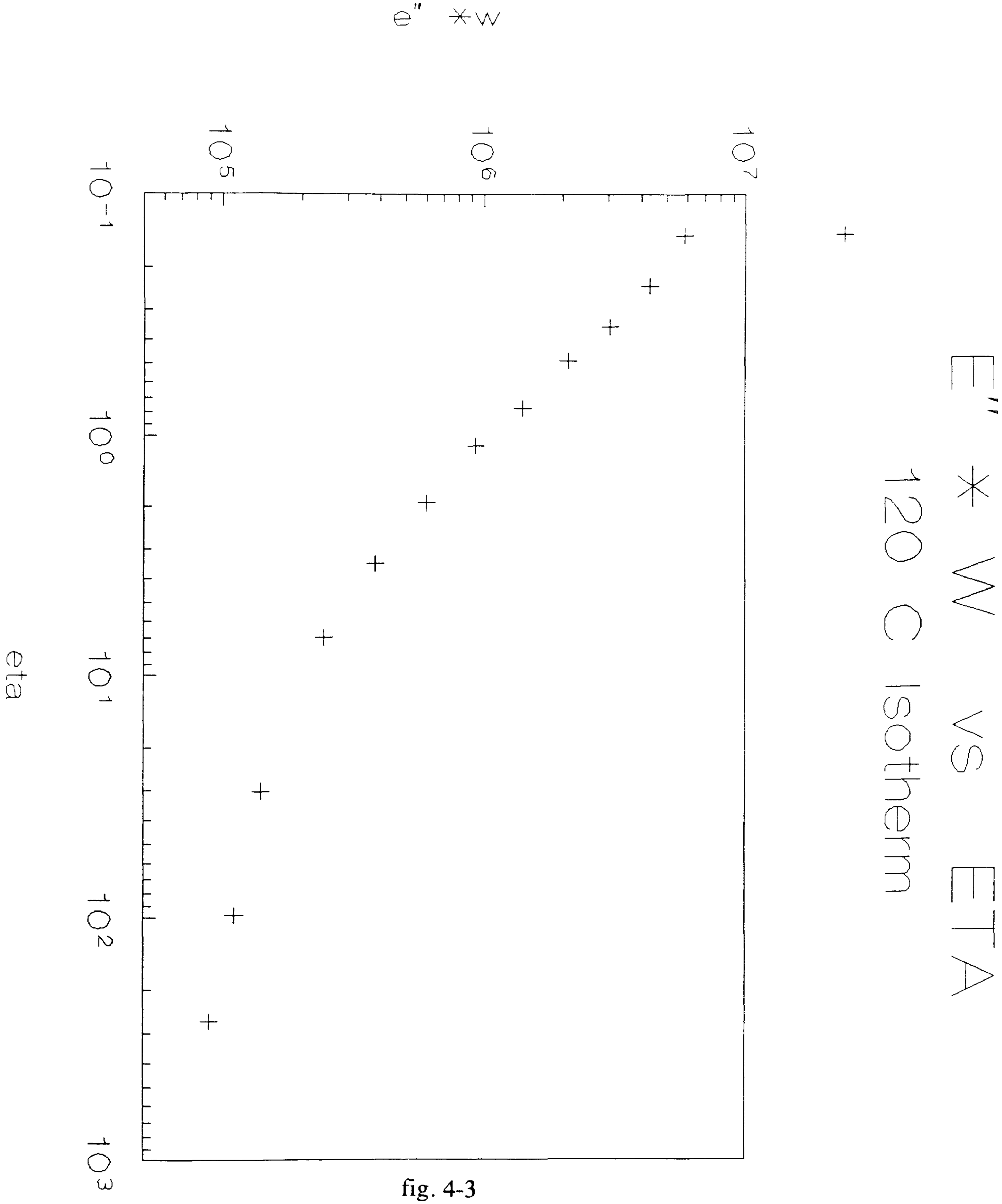
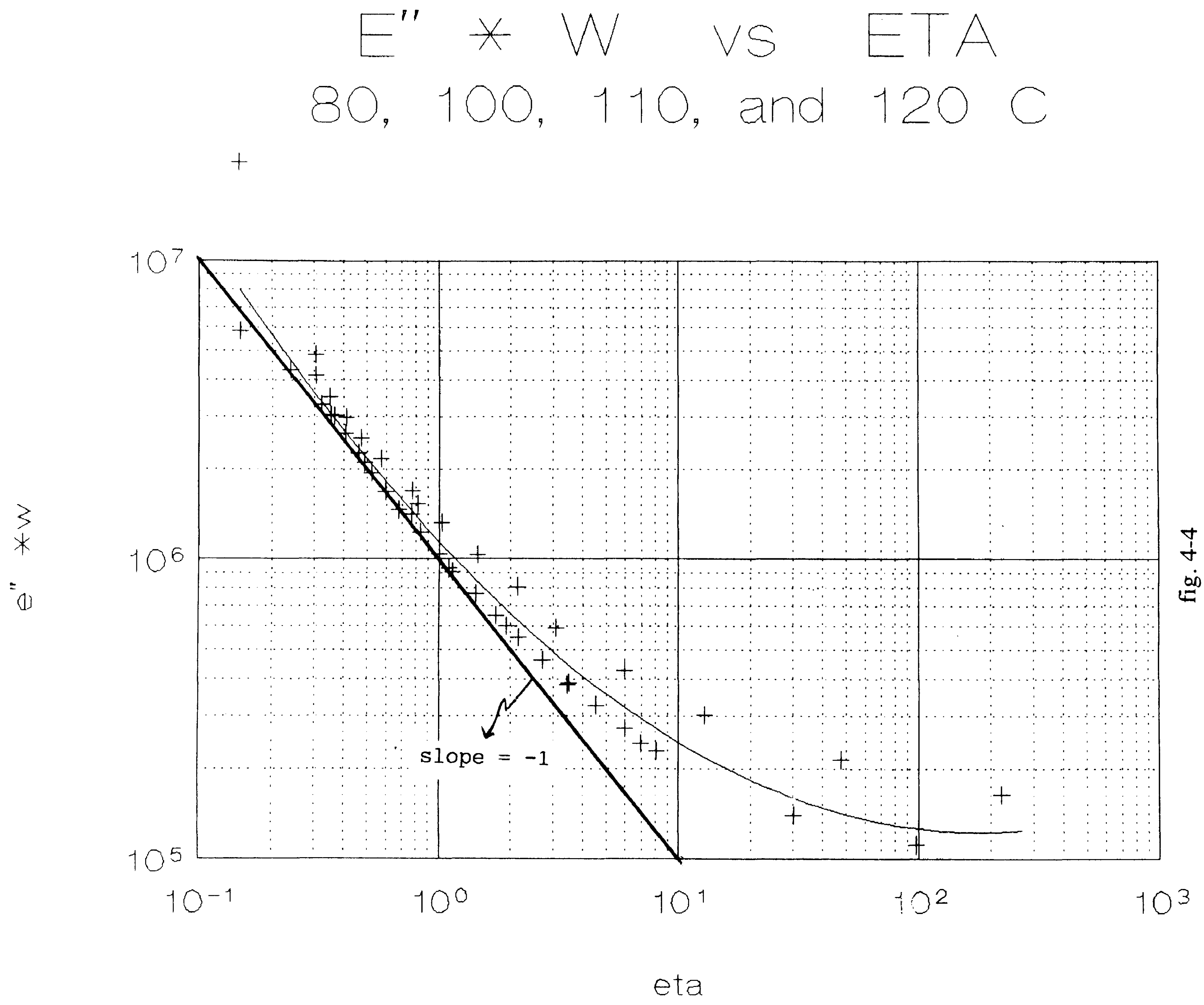


fig. 4-3



E" * W vs ETA

80, 100, 110, and 120 C

fig. 4-4

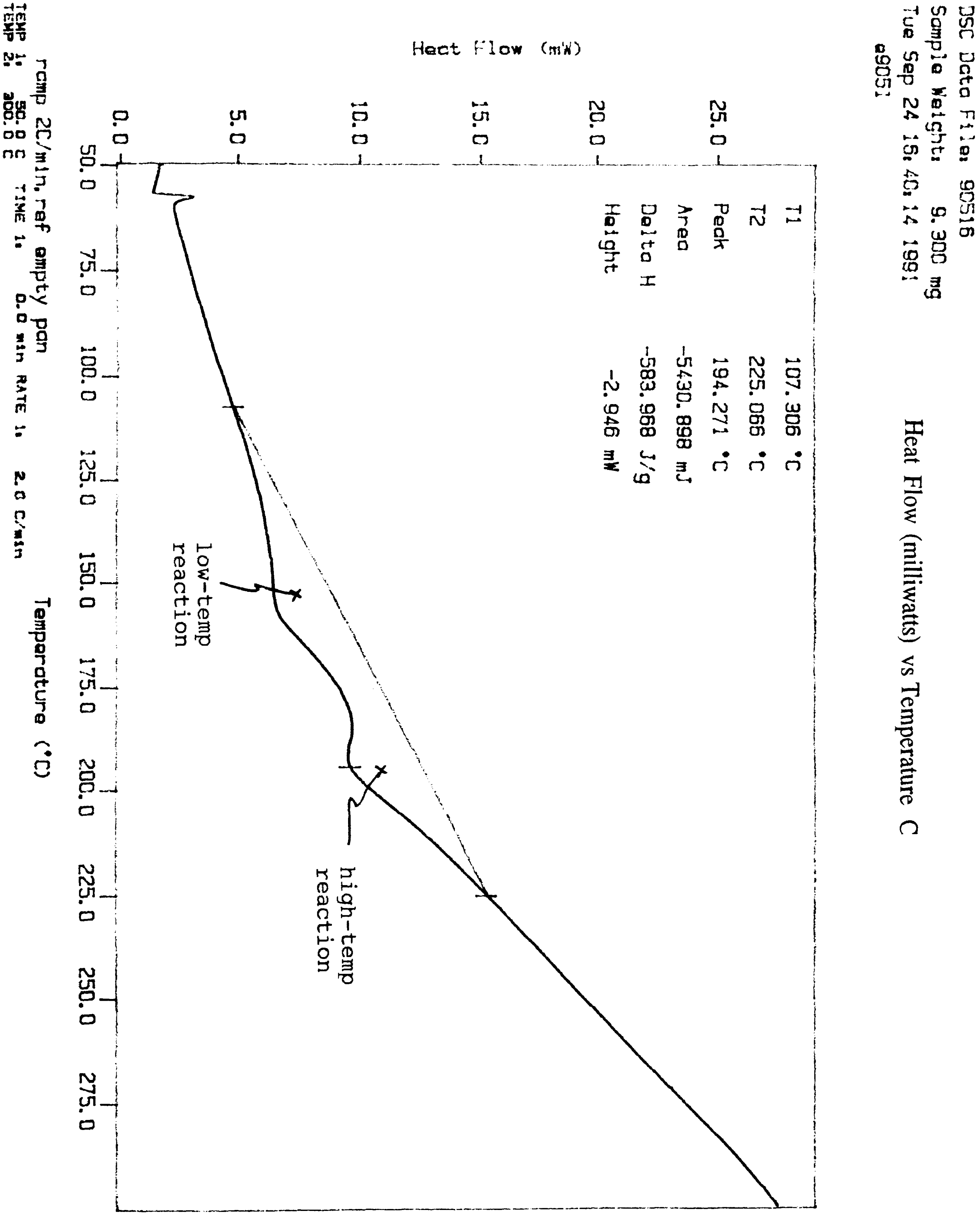

DSC Data File: 90516
Sample Weight: 9.300 mg
Tue Sep 24 15:40:14 1991
a9051
Heat Flow (milliwatts) vs Temperature C
Heat Flow (mW)
0.0
5.0
10.0
15.0
20.0
25.0
T1 107.306 °C
T2 225.066 °C
Peak 194.271 °C
Area -5430.898 mJ
Delta H -583.968 J/g
Height -2.946 mW
low-temp reaction
high-temp reaction
50.0
75.0
100.0
125.0
150.0
175.0
200.0
225.0
250.0
275.0
Temperature (°C)
ramp 2C/min, ref empty pan
TEMP 1: 50.0 C TIME 1: 0.0 min RATE 1: 2.0 C/min
TEMP 2: 300.0 C

fig. 4-5

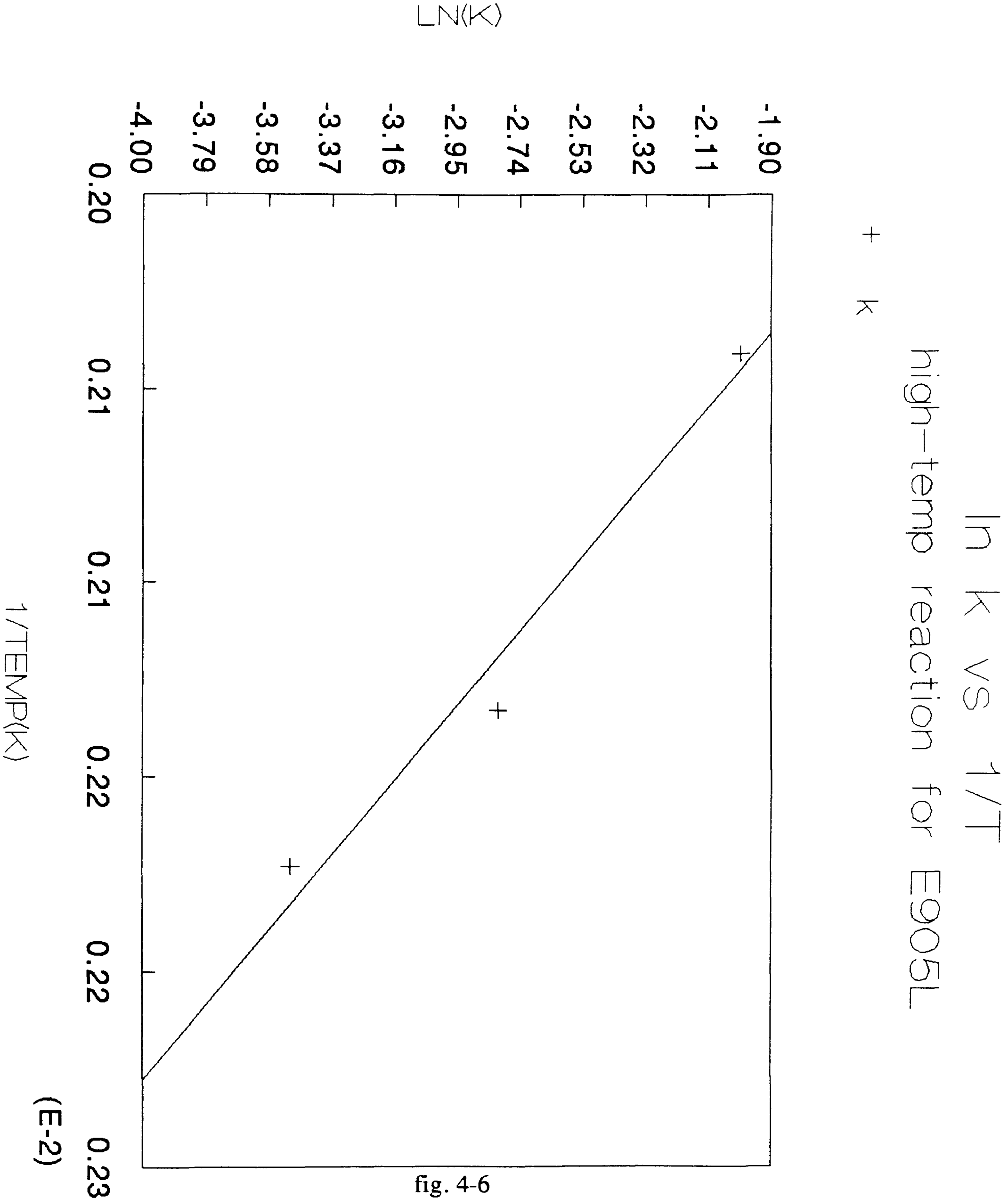

ln k vs 1/T
high-temp reaction for E905L
+ k
LN(K)
-1.90
-2.11
-2.32
-2.53
-2.74
-2.95
-3.16
-3.37
-3.58
-3.79
-4.00
0.20
0.21
0.21
0.22
0.22
0.23
1/TEMP(K)
(E-2)

fig. 4-6

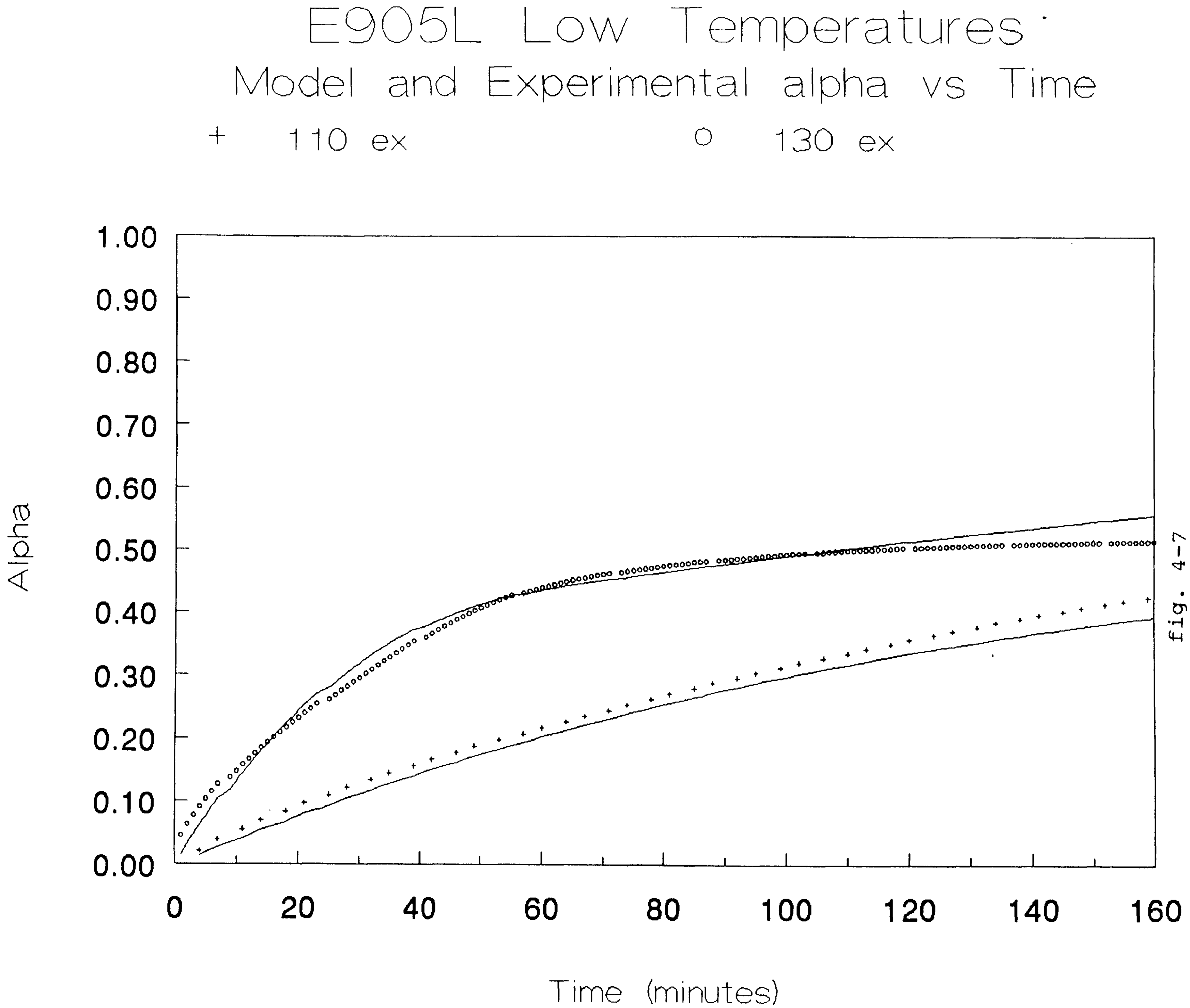

E905L Low Temperatures
Model and Experimental alpha vs Time
+ 110 ex
○ 130 ex
Alpha
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
0
20
40
60
80
100
120
140
160
Time (minutes)

fig. 4-7

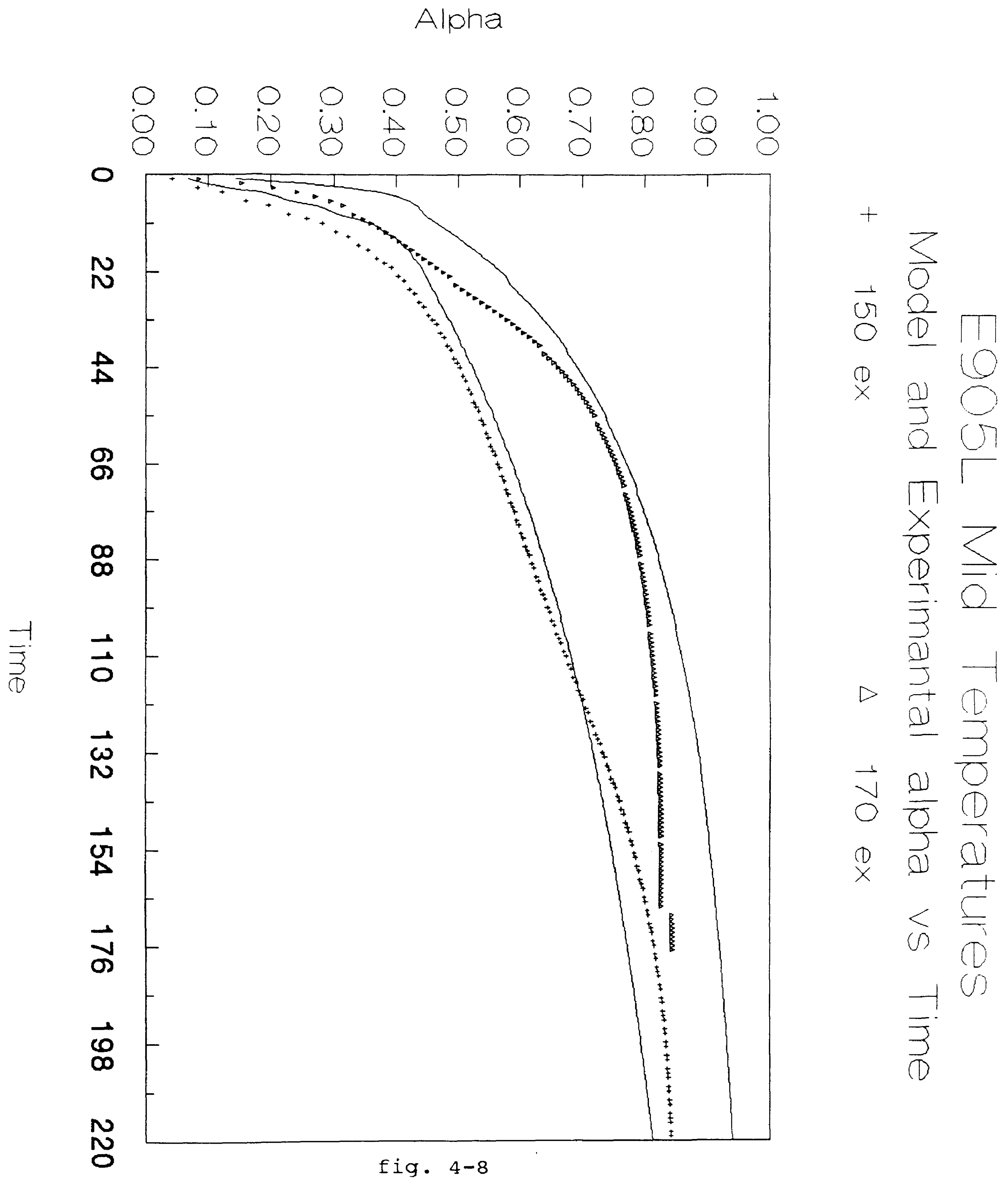

E905L Mid Temperatures
Model and Experimantal alpha vs Time
+ 150 ex
△ 170 ex
Alpha
0.00
0.10
0.20
0.30
0.40
0.50
0.60
0.70
0.80
0.90
1.00
Time
0
22
44
66
88
110
132
154
176
198
220

fig. 4-8

Endnotes for Chapter IV

1. Chiou, P. and Letton, A., "Reaction Kinetics and Chemoviscosity of a Thermoset Exhibiting Complex Curing Behavior", Mechanical Engineering Department, Texas A&M University, College Station, Texas 1990.

CHAPTER V

INTELLIGENT CONTROL of the RTM PROCESS

FDEMS has been shown to be a valuable tool, allowing one to gain molecular and macroscopic insights into the curing process of a polymer resin. Now another, even more useful application for FDEMS is explored. It will serve as the "eyes" for an intelligent, automated closed-loop cure controlling system for the RTM process. An intelligent closed-loop automated control for any composite fabrication process involves the taking of some type of in-situ measurements from a curing composite part. Software then uses the acquired information to analyze the mechanical and chemical state of the resin. Based on its analysis, the software applies a temperature profile that brings the part to the desired degree of cure as quickly as possible.

An intelligent, automated system has several advantages over an operator-applied standard cure cycle. In a standard cure cycle, the temperature ramps and isotherms the resin experiences are based wholly upon time. Differences in the heating rates of different presses and autoclaves as well as resin variations from one batch to another can cause this method of curing to produce final composite parts, cured according to the same schedule, to have widely varied properties. Such inconsistency is due to the fact that the molecular state of the curing resin is ignored by a strict time/temperature scheme.

In a closed-loop, the temperature scheme the part experiences is not based on time or temperature, but on molecular landmarks in the curing resin. Because these critical points may not occur at the exact same time for each part being made, time is not wasted holding a part at some stage when the resin can be advanced. This gives the intelligent, closed-loop process a flexibility that makes it more efficient than a rigid cure cycle.

Additionally, an intelligent closed-loop system produces more consistent parts. The resin's advancement to the next stage of cure is based on its achieving a certain molecular state. Consequently, with each part made, wet-out of the fibers is defined by a common loss value and final cure is defined by a universal degree of cure. This is a much more consistent way to mass produce composite parts then simply subjecting them to the same time/temperature schedule when batch variations and differences in prefabrication handling may be present. Because it reduces fabrication time per part, man hours required and produces more consistent parts, an intelligent closed-loop curing system is a cost effective way to produce composite parts with the high-performance characteristics previously discussed.

An intelligent closed-loop system is composed of a heating/pressure device, such as a press or autoclave, equipment able to gather some sort of in-situ data from the composite part, and a computer with software that collects the measurements, interprets them and is able to control the heating device. The closed-loop system eliminates the need for constant operator supervision.

In this investigation, FDEMS was used to monitor in-situ the curing reaction of a composite part. The author has written a subprogram that makes time/temperature decisions based on FDEMS input and, through a Carver Press, controls the cure of an E905L/graphite composite part. The subprogram is called "controle905l" and it appears in a larger data acquisition program. The main program takes dielectric readings from two sensors and temperature measurements from at least one thermocouple. controle905l then uses this information and criteria described below to make decisions about the time/temperature scheme the part will experience. The temperature that controle905l determines is converted to a decimal number by a portion of code written by A. Williamson. This number is sent to the Carver press. A copy of controle905l appears at the end of this chapter.

Design and Flow of controle905l

When performing an RTM experiment for this investigation, the operator prepares the resin, injection system and mold as previously described in Chapter III. The main program is started prior to resin injection and as soon as the resin is released from the pot, this subprogram takes the part through several stages to final cure. This section describes the logic flow of controle905l, its important variables and the rationale behind the code. All log(e"*w) values specified refer to the 5 kHz signal. controle905l has six main control loops that correspond to different stages in the fabrication process. Entry into these loops is controlled by the variable "e.set."

e.set = 1: The first main control loop determines if and when the part is wet-out. Wet-out can only occur in one manner, when both sensors have registered three consecutive readings of log(e"*w) >5.9. If one sensor's value drops below 5.9 prior to it's counter variable exceeding two, the counter variable is reset to 0. 5.9 is the wet-out value because fiberglass or other non-resin foreign material will not give such a high reading, only resin against the sensor's active face will achieve this value. Three consecutive readings eliminate the possibility of a random spike satisfying wet-out conditions. When both sensors show wet-out, a timer is set that delays progress to the next stage by 4 minutes. The delay ensures that before the resin is advanced, it has additional time to fully wet out the fiber in the mold, not just cover the sensors which lie on the bottom base plate.

controle9051 maintains the mold at 100 C during e.set = 1. This is done to lower the viscosity upon the resin's entrance into the mold and further facilitate the fiber saturation process.

In the case of one sensor achieving wet-out and the other not, which indicates that wet-out is not complete, the 100 C hold is maintained until the e" value of the wet sensor falls to one-half the wet-out value, which is log(e"*w) = 5.6. Such a drop would indicate an increase in degree of cure and thus a decrease in viscosity. Accordingly, a slow ramp of 1 C per minute is then outtemped to the mold with a maximum possible value of outtemp being 121. This is done in order to lower the resin viscosity and maximize the chance of the dry sensor seeing resin, i.e. to achieve full impregnation. If the dry sensor wets out or the mold temperature reaches 117 C, then the next stage (e.set =2) is entered into.

e.set =2: e.set =2 brings the part to a 121 hold. It outtemps 121, waits for the actual temperature to reach 117 C, initializes a timer variable when this temperature is reached and then sets e.set =3. The beginning of the 121 hold is defined as the time when the mold temperature reaches 117 C. This is because the temperature slowly creeps the last few degrees to 121 C and these few degrees do not significantly effect the resin behavior for which the sensor is looking.

e.set =3: This loop outtemps 121, thereby maintaining the 121 C hold reached in e.set =2, and determines the end of this stage. British Petroleum recommends whenever E905L is cured, a 121 C hold be included for 90 minutes and that gel be verified during this time. The reason for this warning is to prevent dangerous exotherms, possibly explosive if the resin is in a sealed container, such as a mold.

Based on these recommendations, the end of e.set =3 is triggered by the occurrence of one of two conditions. The first is when log (e"*w) drops below 4.8 for four consecutive readings. A value greater than 4.8 causes the counter variable. e.wet.drop%, to be reset to zero. Again, multiple readings beyond the critical point prevent a random spike from prematurely terminating this important stage. Figure 5-1 is a graph of alpha and log eta vs log (e"*w) for a 100-minute 121 C isothermal hold. An examination of this graph provides insights into the manufacturer's recommendations. During this time the viscosity of E905L achieves a value of 2.0e2 P, its gel point. This occurs at approximately 80 minutes and corresponds to a log(e"*w) value of 4.95. Thus, by the time the resin has achieved a low enough loss value to signify the end of the 121 C hold, it has definitely achieved chemical gel.

The reason that a 121 C hold may defuse an explosion is also apparent in figure 5-1. After an RTM injection and fiber wet-out, α of E905L is typically in the 0.04 - 0.08 range. If a newly saturated part were to be ramped to a high temperature, say 177 C, and cured, the barely reacted resin would exotherm violently. This phenomenon has been verified in our laboratory. One attempt to perform a 177 C FDEMS run on freshly mixed resin ended quickly when the resin combusted.

However, once the resin reaches a molecular state equivalent to 100 minutes of cure at 121 C, namely log(e"*w) =4.8, α has risen to approximately 0.42. A significant portion of E905L's heat of reaction has been bled off during this hold. Thus, when log(e"*w) reaches 4.8, regardless of how long the resin has actually been at 121 C, the operator can be sure that gel has occurred and the resin's degree of cure is high enough to safely permit further advancement. The above discussion is illustrative of the flexibility and efficiency of an intelligent cure-monitoring system. Rather than blindly waiting for 90 minutes to pass, as recommended by British Petroleum, the sensor identifies the equivalent molecular state. This state may occur at different times in the fabrication of different composite parts but the intelligent control system will recognize this, and applies the temperature scheme accordingly.

The second condition that signals the end of this intermediate hold is simply the passing of 90 minutes. This is a precautionary condition. In the case of both sensors failing, a 90-minutes delay at 121 C ensures that the molecular landmarks discussed above are achieved. If one of these two conditions is met, e.set is increased to 4.

e.set =4: At this point, the resin can safely be heated to higher temperatures and the goal now is to achieve the desired level of cure as quickly as possible. e.set=4 ramps the part to its final hold of 177 C. The outtemp value is 180 in order to compensate for a slight heat lag at higher temperatures. The beginning of the 177 C hold is defined as when the actual temperature of the part reaches 174 C; the rationale being the same as that in e.set =2 to justify the 121 C hold beginning at 117 C. When 174 C is achieved, a timer variable is initialized and then e.set is set equal to 5.

e.set =5: This stage tests for the end of the run while maintaining the 177 C hold. Again, one of two conditions will trigger the end of this stage. The first is when the slope of the 5 kHz signal achieves a value of zero. The slope is defined as the quantity (de"/dtime)/e". The data points n and (n-2) are used in the slope calculation, where n is the most recently measured data point. The dtime quantity has the units of seconds. Since there is background noise, it is not realistic to expect a slope of zero over a short time period. Accordingly, four consecutive occurrences of the absolute value of (de"/dtime)/e" < 0.000545 qualifies as a zero slope.

After 20 minutes of final hold, the computer calculates the value of (de"/dtime)/e" each cycle. This calculation is delayed 20 minutes so that the inflection of the loss signal as log(e"*w) goes through a maximum, due to the increased fluidity caused by rapid heating, is not interpreted as a zero slope.

Every time the magnitude of (de"/dtime)/e" exceeds 0.000545 then the counter variable, e.shutdown%, is reset of zero, despite its previous value. When e.shutdown% = 4, e.set is set to 6.

Figure 5-2 is a plot of the (de"/dtime)/e" slope, model-generated alpha and experimental alpha vs time for an isothermal E905L cure at 172 C. The experimental alpha curve is actually a 170 C hold, which explains why it follows the shape of the 172 C model but lies below it. 172 C is the closest temperature to 177 C at which a successful isotherm could be run without causing a runaway exothermic reaction. This graph indicates a series of four consecutive slopes below 0.000545 corresponds to an alpha of approximately 0.75. This end-of-cure determination can serve as a tuning mechanism for the final hold of RTM runs.

A higher alpha than 0.75 may be achieved in several ways. One is to decrease the magnitude of the zero slope allowance. Decreasing this magnitude will lead to a higher degree of cure, however, the smaller the zero slope requirement, the more likely its magnitude will be exceeded by noise prior to four consecutive occurrences. Also, by this time, the reaction proceeds very slowly, due to the diffusion limitations on the movement of the molecules as the resin approaches the glassy state.

A postcure is another technique to achieve a higher final part alpha. A post cure simply consists of demolding the mostly cured part and then holding it at a higher temperature than its final hold for a set period of time.

A lower end-of-cure alpha may be attained by increasing the magnitude of the zero slope requirement. Thus, causing the run to terminate when the resin is at an alpha lower than 0.75.

The second condition that terminates the run is the passing of two hours. This is a precaution in case of sensor malfunction, which would cause the hold continue indefinitely. This condition also protects against a very noisy sensor that would never show a "zero" slope. When one of these two conditions is met, the value of e.set becomes 6.

e.set =6: e.set =6 merely outtemps 25 C until data collection is terminated.

Fabrication of a Composite Part with "controle9051"

This section details and discusses the fabrication of an actual composite part by the

RTM process described in this paper, with controle9051 controlling the run. The run is known as HR101191.DAT.

Fiber, resin and mold preparation for HR101191.DAT followed the outline in Chapter III. 28 plies of 2-dimensionally woven graphite cloth, weighing 232 grams, composed the fiber preform. The plunger used was .5" thick, resulting in a part of the same thickness. Three sensors were inserted into the lay-up, underneath the fiber preform. Sensor #1 was located next to the left injection port, sensor #2 lay directly beneath the center exit hole of the plunger and sensor #3 was next to the right injection port. Sensors 1 and 2 were used, #3 was the backup. Two thermocouples were present as well. Thermocouple #1 was situated between sensors 1 and 2 while thermocouple #2 sat between sensors 2 and 3.

Output for both sensors appears as figures 5-3 and 5-4 in log(e"*w) {9 frequencies} and temperature vs time form. Figure 5-3 is the output from sensor #1 and thermocouple #1. Figure 5-4 is the output from sensor #2. The temperature it depicts is the value of the variable "outtemp." The graphs have been divided into three zones for ease of discussion.

The signal in zone #1 is that of the sensors experiencing the dry mold coming to the injection temperature then the initial sensor/resin contact. During most of this time, the resin was being degassed and final run preparations were being made.

The drop in the loss signal at time =32 minutes is a vacuum being applied to the mold. At time =39 minutes, system set-up was complete and the resin was released from the pressure pot immediately after the completion of a frequency-measurement cycle. At time =42 minutes, the resin had covered the sensors. Both graphs show a jump in all frequencies of nearly 3 orders of magnitude at this time.

The first reading of the wet sensors is often significantly slower than the previous dry-sensor or subsequent wet-sensor readings. This is because the Hewlett-Packard Bridge gets temporarily delayed by the dramatic change in capacitance. The hang-up can cause the cycling and measuring of frequencies to take as long as 4 minutes, as compared to a normal speed of about 40 seconds. The first reading after injection took about two minutes, during which time the resin exited the mold via the top call plate. At time =44 minutes the valve to the vacuum line was closed and the vacuum pump was turned off.

As can be seen in figures 5-3 and 5-4, the signal of the initial resin/sensor contact is well above log(e"*w) =5.9, the minimum value of a wet sensor. This value was held for the requisite three readings and then the four minute hold began. This hold allows the resin to completely wet-out the fibers. After the four minutes elapsed, the requirement for part saturation was met and the ramp to 121 C was begun.

Zone #2 depicts the part being ramped to 121 C and the subsequent hold. At time = 78 minutes, the temperature reached 117 C and the 121 hold begins. Figures 5-5 and 5-6 are graphs of eta and alpha, respectively, vs time, up through the end of this intermediate stage. For both graphs, the time axis is that of HR101191.dat.

Figure 5-5 shows eta from the time of injection to the gel point of E905L. The gel point occurs at time =115 minutes, 15 minutes prior to the end of the 121 C hold. This accomplishes with one of the goals of the this stage, to ensure chemical gel of the resin.

Figure 5-6 depicts the degree of cure of E905L from initial mixing through the end of the 121 C hold. At the end of the injection process, time =65 minutes, alpha =0.05. However, by the end of the intermediate hold, alpha has increased to approximately 0.36. Thus we see how the 121 C hold has allowed the resin system to slowly release a considerable amount of heat.

At time =122 minutes, log(e"*w) first drops below 4.8. This is the value that defines the end of the 121 C hold. Four ensuing readings remain below the critical point and the 121 C hold is over. Subsequently, the part is safely ramped to the final hold at 177 C.

Zone #3 includes the ramp to 177 C and the final hold itself. Figures 5-3 and 5-4 show that the loss signal experiences two local maximums before settling into its steadily declining final pattern. The first local peak is due to the sudden temperature increase of the ramp. This ramp causes an increase in fluidity and thus a rise in the e" values. As this peak begins to subside, however, a second peak appears. This peak begins when the temperature is approximately 165 C. The temporarily increased fluidity reflected by the second peak is due to the heat from the high-temp reaction. Which has primarily been latent until this point.

At time =159 minutes, the temperature has reached 174 C and the final hold has begun. After a delay of twenty minutes, the slope is calculated and compared to the zero slope requirement after every cycle. The resin quickly meets the criteria for a zero slope and after four consecutive occurrences, at time =185 minutes, the value of outtemp is set equal to 25 until the data collection program is terminated.

Figure 5-7 depicts alpha vs time for the final ramp and hold of HR101191.DAT. The theoretical degree of cure reached is 0.76, based on the model. This predicted value is in good agreement with the experimental value indicated by the sensor from the plot of slope vs degree of cure (fig. 5-2). As can be seen from 5-7, a high degree of cure, such as 0.95, would require an extensive hold at 177 C. A postcure at a higher temperature, such as 205 C, would achieve a high alpha value much more efficiently.

Once the part is complete and the data collection has ended, the press is allowed to cool for a few hours. After which the part is carefully demolded.

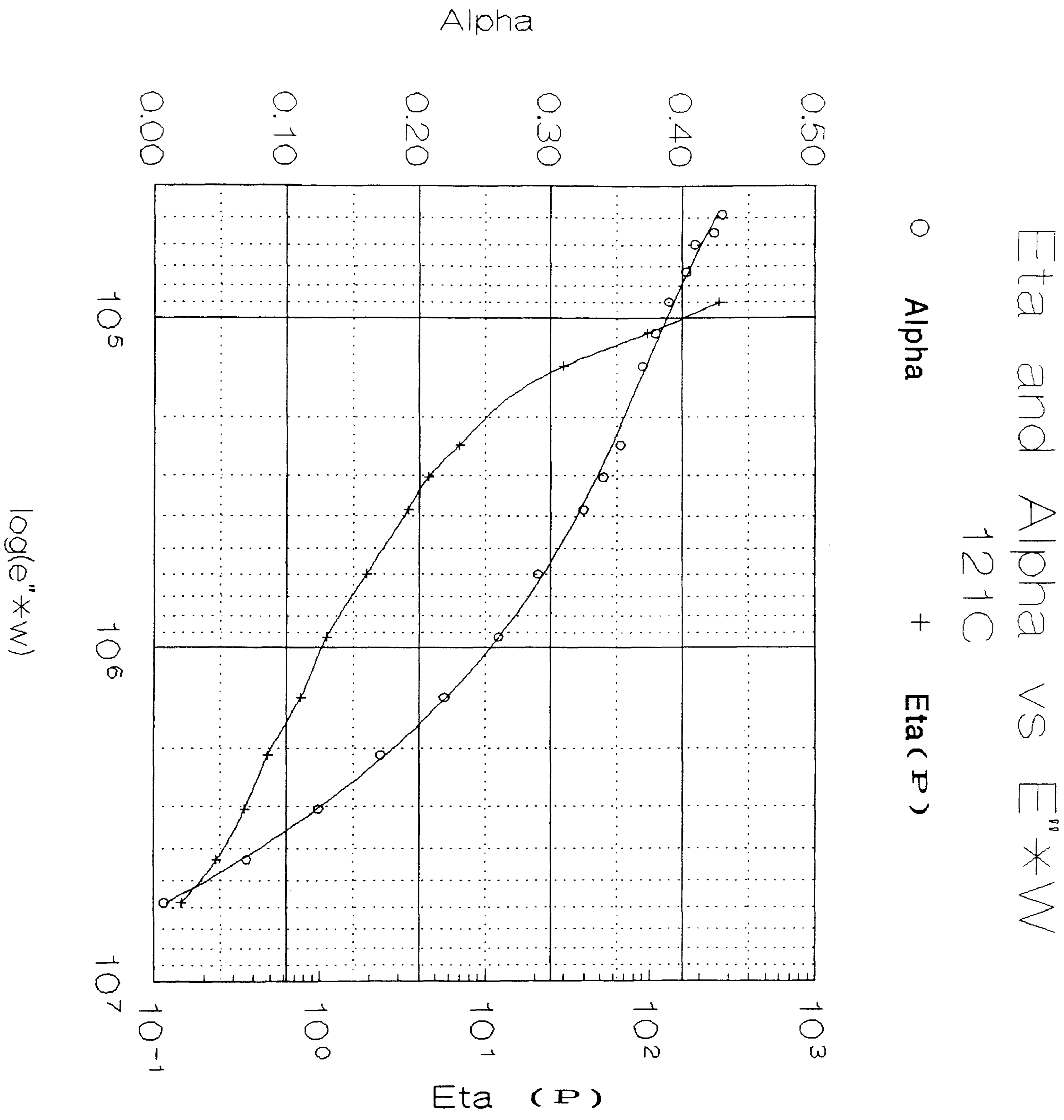

Eta and Alpha vs E"*W
121C
○ Alpha
+ Eta(P)
Alpha
0.00
0.10
0.20
0.30
0.40
0.50
Eta (P)
10^{-1}
10^{0}
10^{1}
10^{2}
10^{3}
log(e"*W)
10^{5}
10^{6}
10^{7}

fig. 5-1

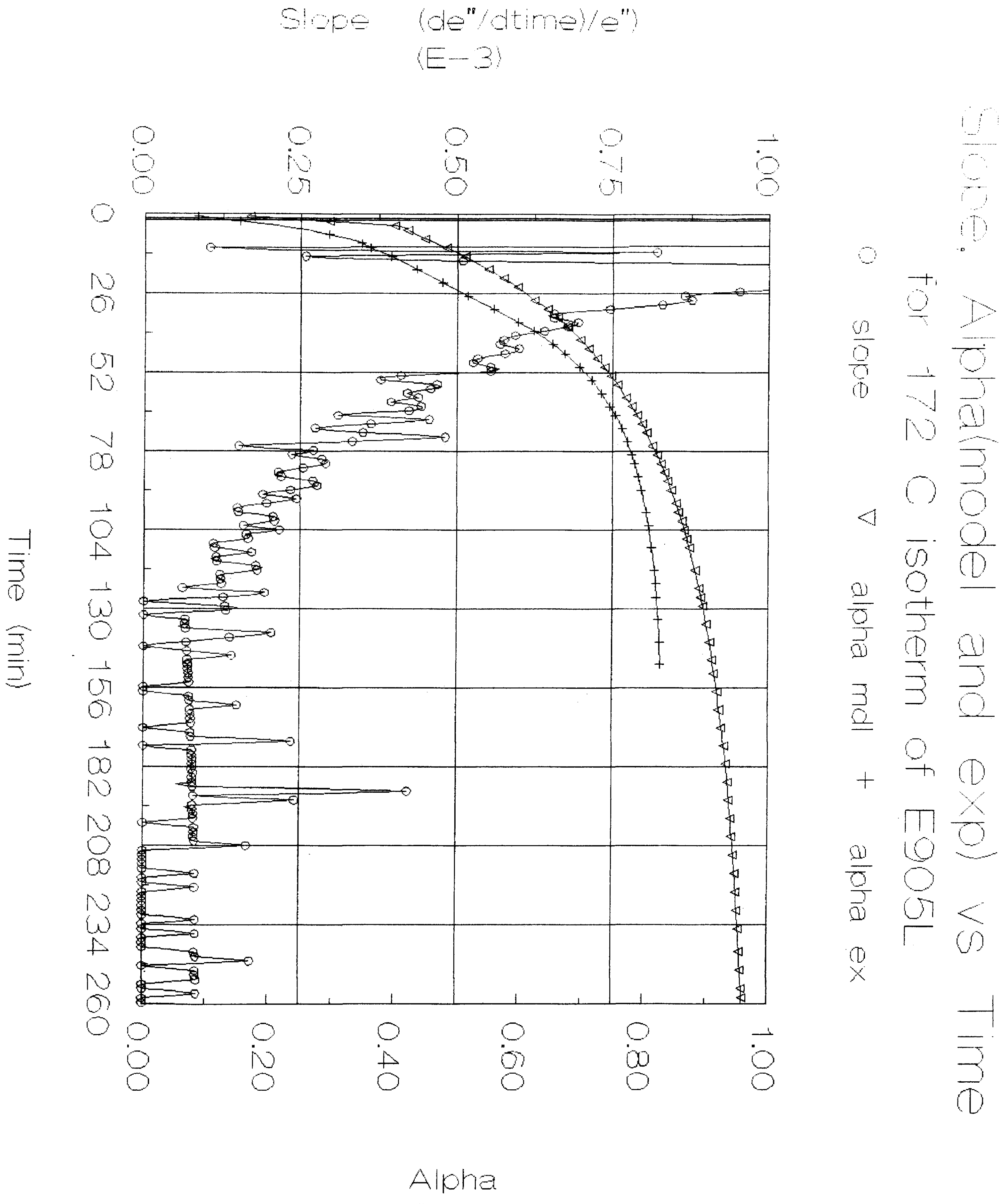
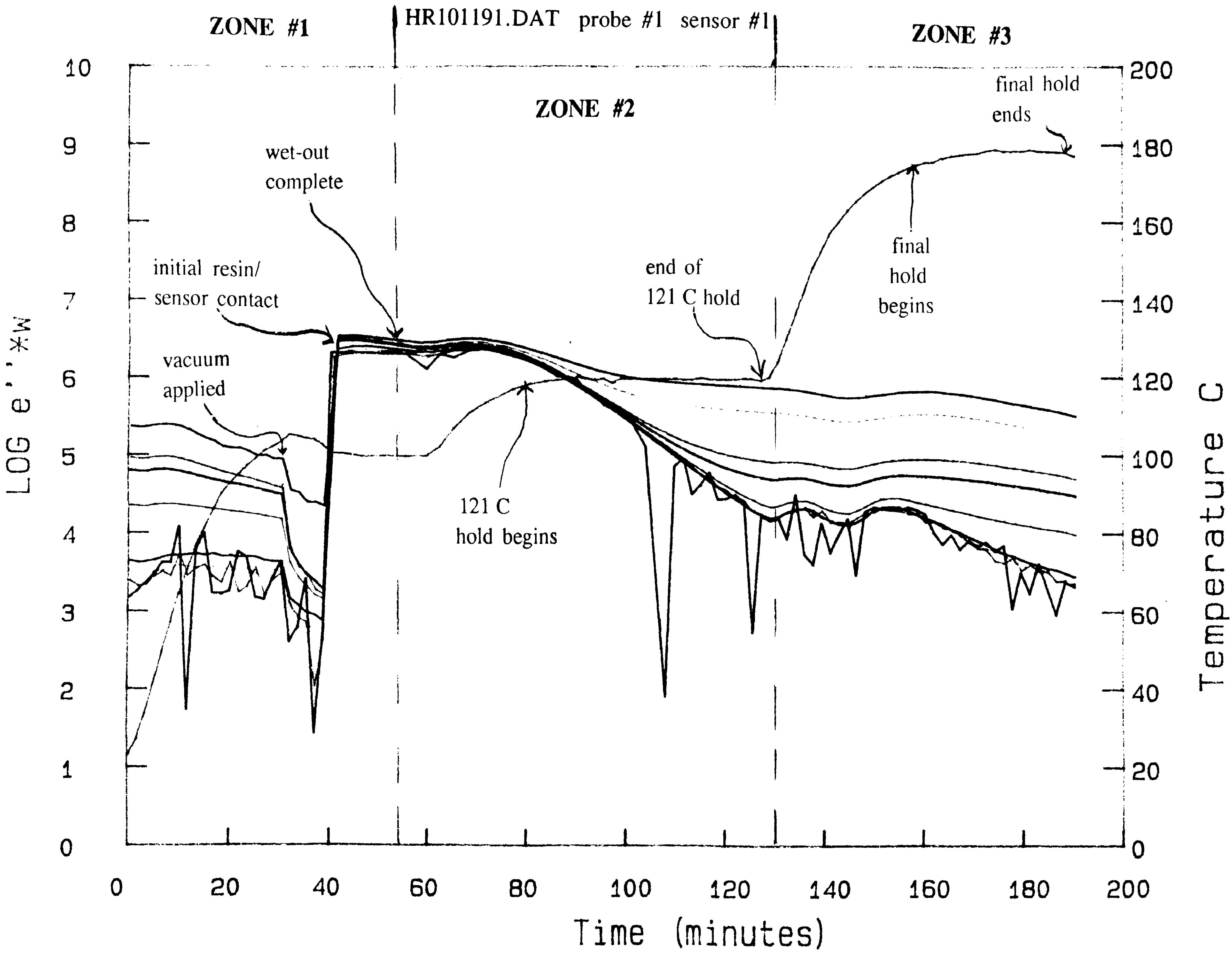
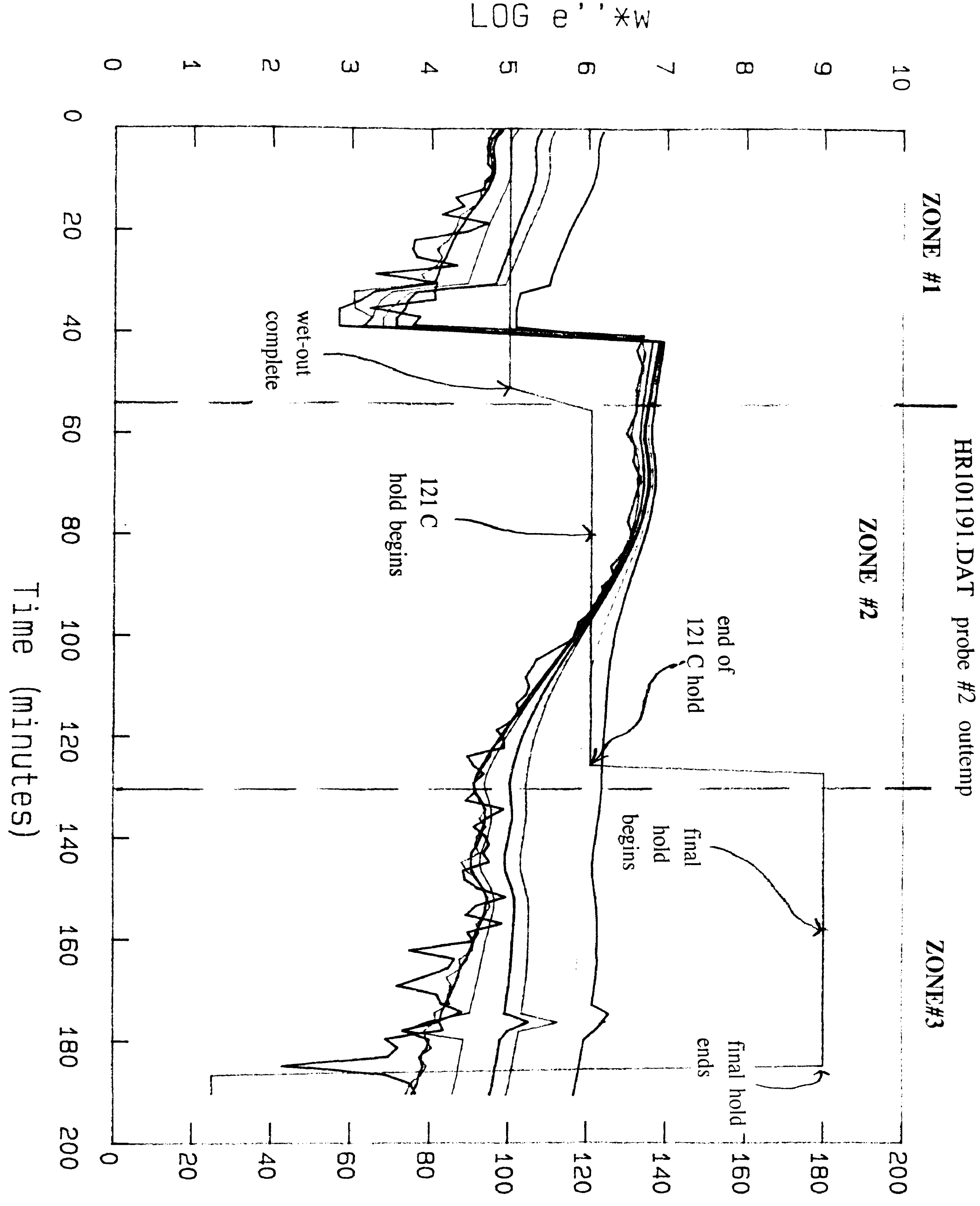
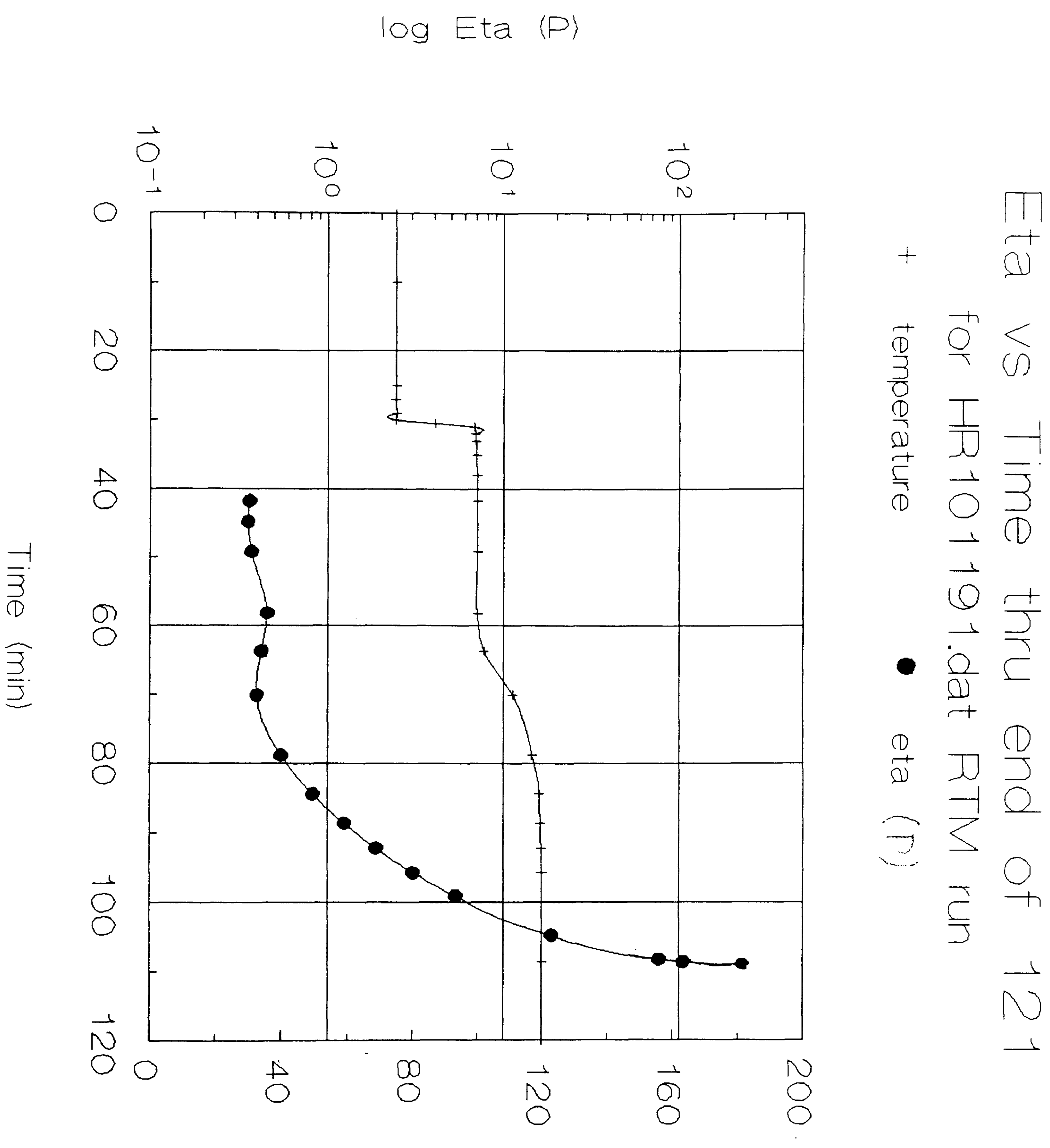

Slope, Alpha(model and exp) vs Time
for 172 C isotherm of E905L
○ slope
∇ alpha mdl
+ alpha ex
Slope (de"/dtime)/e")
(E-3)
0.00
0.25
0.50
0.75
1.00
0
26
52
78
104
130
156
182
208
234
260
Time (min)
0.00
0.20
0.40
0.60
0.80
1.00
Alpha

fig. 5-2


ZONE #1
HR101191.DAT probe #1 sensor #1
ZONE #2
ZONE #3
final hold ends
wet-out complete
final hold begins
initial resin/ sensor contact
end of 121 C hold
vacuum applied
121 C hold begins
LOG e''*W
0
1
2
3
4
5
6
7
8
9
10
Temperature C
0
20
40
60
80
100
120
140
160
180
200
Time (minutes)
0
20
40
60
80
100
120
140
160
180
200


HR101191.DAT probe #2 outtemp
ZONE #1
ZONE #2
ZONE#3
LOG e''*w
0
1
2
3
4
5
6
7
8
9
10
Time (minutes)
0
20
40
60
80
100
120
140
160
180
200
Temperature C
0
20
40
60
80
100
120
140
160
180
200
wet-out complete
121 C hold begins
end of 121 C hold
final hold begins
final hold ends



Temperature C

fig. 5-5

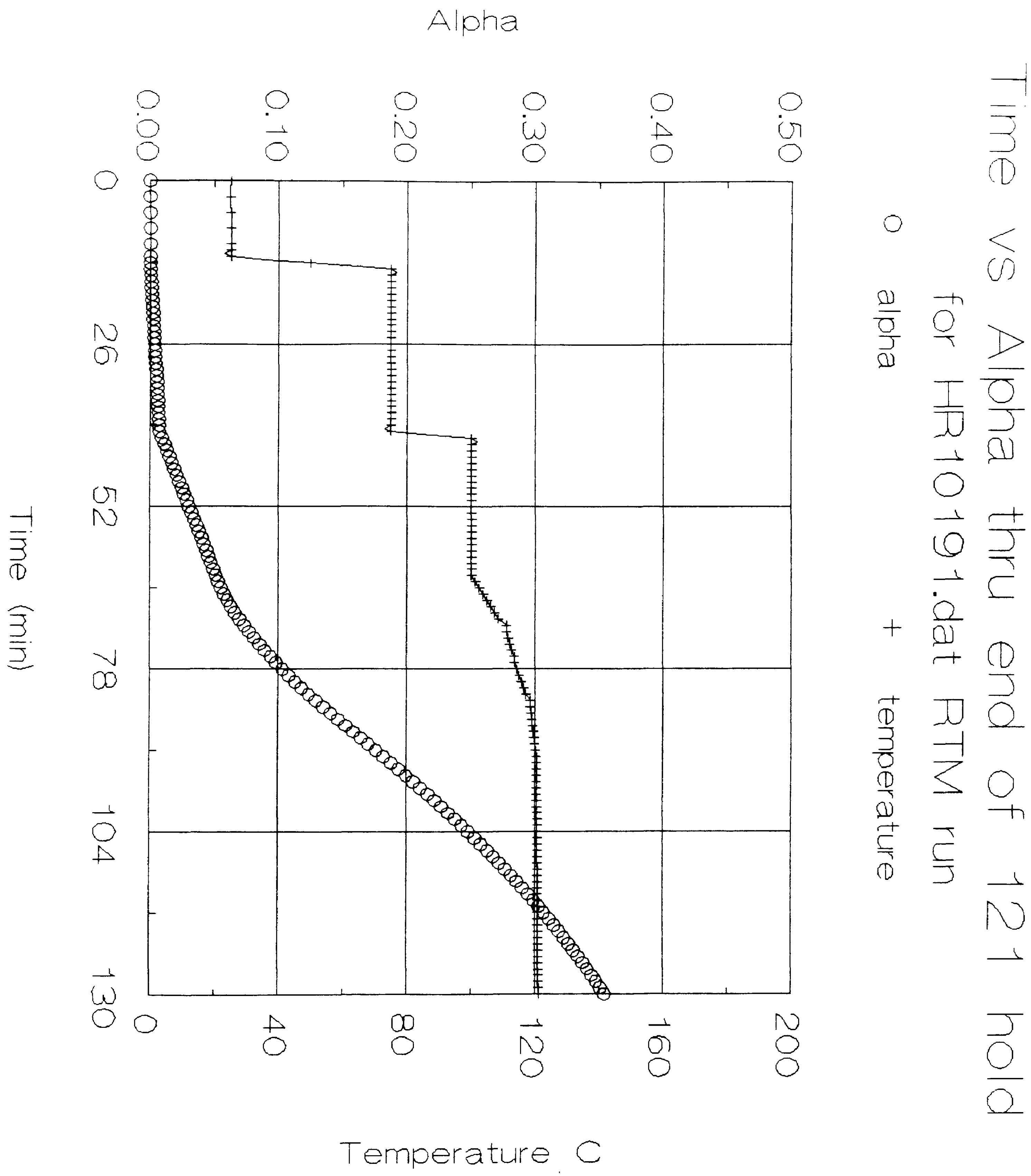

Time VS Alpha thru end of 121 hold
for HR10191.dat RTM run
○ alpha
+ temperature
Alpha
0.00
0.10
0.20
0.30
0.40
0.50
0
26
52
78
104
130
Time (min)
0
40
80
120
160
200
Temperature C

fig. 5-6

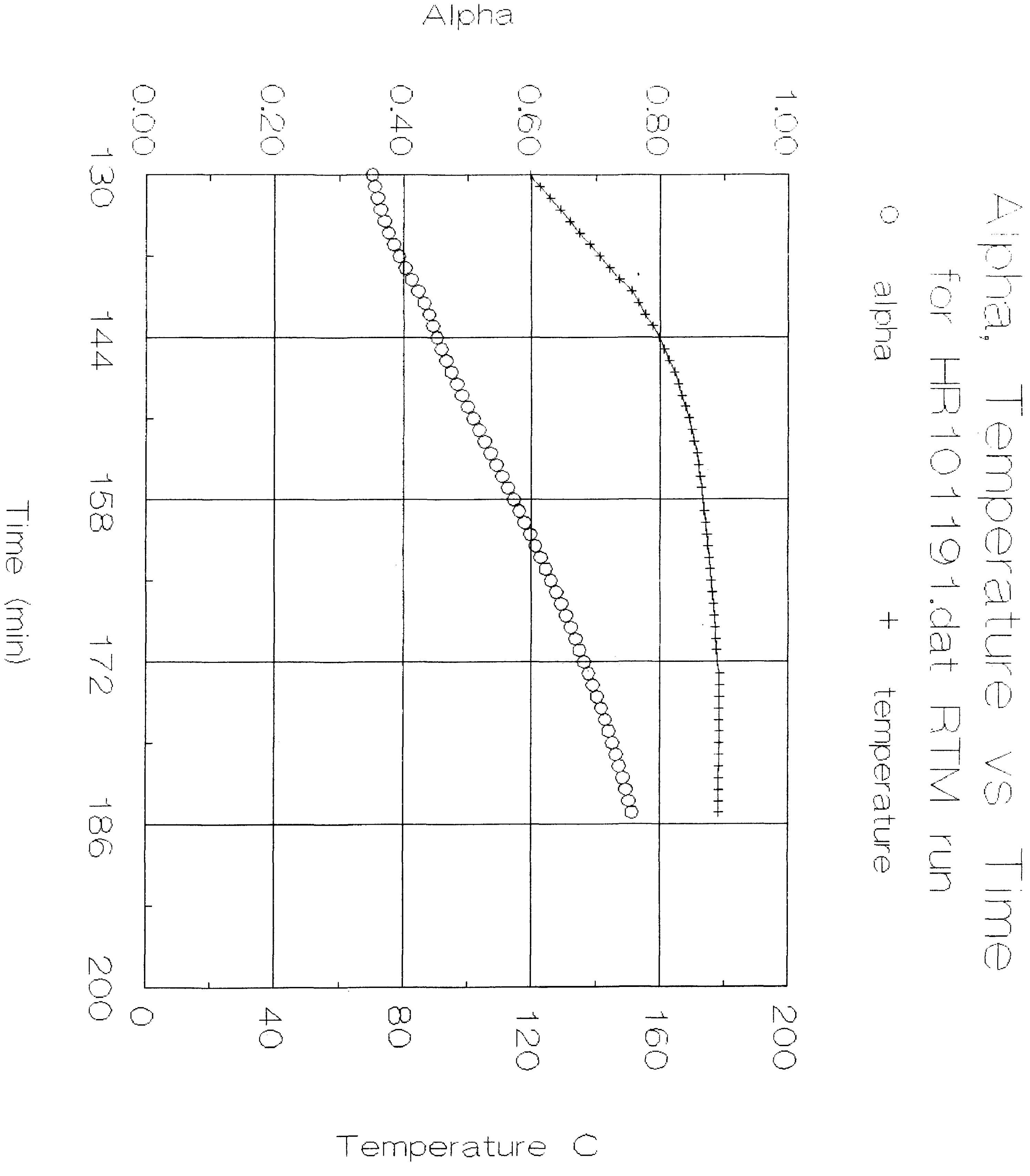

Alpha, Temperature VS Time
for HR101191.dat RTM run
○ alpha
+ temperature
Alpha
0.00
0.20
0.40
0.60
0.80
1.00
Time (min)
130
144
158
172
186
200
Temperature C
0
40
80
120
160
200

fig. 5-7

Subprogram "controle9051"

```
REM ----------------------------------------------------------------------


REM This sub controls the rtm process for E905L resin
SUB controle9051

REM ***********  e.set = 1 during beginning of run and injection ***********
REM This portion of code is the e.set = 1 portion.  It checks both sensors
REM for wet-out, where wet-out is defined as 2 consec. readings of e'' > 24
REM (at 5kHz). If only one sensor wets out and its e'' value drops by 50%
REM (ie. to 12) then a slow ramp (1 C/min) is outtemped to 121 until the
REM temp = 117C (outtemp stops increasing at 121) or the second sensor wets
REM out. If both sensors wet-out then there is a 4-minute wait and then
REM e.set = 2.

IF e.set = 1 THEN
  outtemp = e.inj.temp
  IF e2#(count%, 5, 1) > 24 THEN e.wet1% = e.wet1% + 1
  IF e2#(count%, 5, 1) < 24 THEN e.wet1% = 0
  IF e2#(count%, 5, 2) > 24 THEN e.wet2% = e.wet2% + 1
  IF e2#(count%, 5, 2) < 24 THEN e.wet2% = 0
  IF e.wet1% > 2 AND e.wet2% > 2 THEN
    sat.time = run.time(count%, 1, 1) / 60
    e.wet3% = 3
  END IF

  IF e.wet3% = 3 THEN
    IF run.time(count%, 1, 1) / 60 > sat.time + e.del.time THEN e.set = 2
  END IF

  IF (e.wet1% > 2 AND e.wet2% < 2) OR (e.wet1% < 2 AND e.wet2% > 2) THEN
    IF e2#(count%, 5, 1) < 12 OR e2#(count%, 5, 2) < 12 THEN
      occurences% = occurences% + 1
      IF occurences% = 1 THEN
        e.ramp.time = run.time(count%, 1, 1) / 60
        occurences% = 2
      END IF
      outtemp = outtemp + (INT(run.time(count%, 1, 1) / 60 - e.ramp.time))
      IF outtemp > 121 THEN outtemp = 121
      IF temp(count%, 1) > 117 THEN e.set = 2
    END IF
  END IF
END IF


REM ----------------------------------------------------------------------
REM -----------------------------e.set = 2 while waiting for temp to------
IF e.set = 2 THEN                    'reach the 121 hold ---------------------
  outtemp = 121
  IF temp(count%, 1) > 117 THEN
    interm.time = run.time(count%, 1, 1) / 60
    e.set = 3
    outtemp = 121
  END IF
END IF
```

```
REM ========================================================================
REM ============================= e.set = 3 signals the end of the 121 hold
IF e.set = 3 THEN              '===== either by dropping below a specified  e"
  outtemp = 121                '===== point (e.ew) or exceeding spec. time.
  IF e.wet.drop% < 4 THEN
    IF e2#(count%, 5, 1) < e.ew THEN e.wet.drop% = e.wet.drop% + 1
    IF e2#(count%, 5, 1) > e.ew THEN e.wet.drop% = 0
    IF run.time(count%, 1, 1) / 60 > interm.time + e.121wait THEN e.set = 4
  END IF

  IF e.wet.drop% = 4 THEN e.set = 4
END IF


REM -------------------------------------------------------------------------
REM ----------------------------e.set= 4 sets the clock for the final 177 hold
IF e.set = 4 THEN
  outtemp = 210
  IF temp(count%, 1) > 174 THEN
    final.hold = run.time(count%, 1, 1) / 60
    e.set = 5
  END IF
END IF

REM ========================================================================
REM =========================== e.set=5 tests for end of run either by time
IF e.set = 5 THEN             '=== or by dedt/e reaching .000545 (5kHz, sensor1)
  outtemp = 180
  IF end.of.cure = 1 THEN
    IF run.time(count%, 1, 1) / 60 > final.hold + 20 THEN
      IF e.shutdown% < 4 THEN
        IF ABS(((e2#(count% - 2, 5, 1) - e2#(count%, 5, 1)) / (run.time(count
 2, 1, 1) - run.time(count%, 1, 1))) / e2#(count%, 5, 1)) <= e.dedt THEN e.sh
own% = e.shutdown% + 1

        IF ABS(((e2#(count% - 2, 5, 1) - e2#(count%, 5, 1)) / (run.time(count
 2, 1, 1) - run.time(count%, 1, 1))) / e2#(count%, 5, 1)) > e.dedt THEN e.shu
wn% = 0

        IF run.time(count%, 1, 1) / 60 > final.hold + e.final.time THEN e.set
6
      END IF

      IF e.shutdown% = 4 THEN e.set = 6

    END IF
  END IF

  IF end.of.cure = 2 THEN
    IF run.time(count%, 1, 1) / 60 > final.hold + e.final.time THEN e.set = 6
  END IF
END IF

REM ----------------------------------------------------------------------
REM ---------------------this brings temp down to 25 C after run has ended
IF e.set = 6 THEN
  outtemp = 25
END IF
REM ----------------------------------------------------------------------


WRITE #1, outtemp

addr = 768
b(2) = -1300
b(3) = -1695
```

```
m(2) = 17.54
m(3) = 20!

FOR C% = 2 TO 3

d(C%) = (outtemp * m(C%)) + b(C%)
d = d(C%)
IF outtemp < 80 THEN d = 0

61020 XH% = INT(d / 256)            'work out high byte
61030 XL% = d - 256 * XH%           'remainder = low byte

OUT addr + (C% * 2), XL%            'write low byte to D/A
61050 OUT addr + (C% * 2) + 1, XH%  'write high byte & load D/A

NEXT C%
e.no.cont:
END SUB
```

CHAPTER VI
CONCLUSIONS

FDEMS is proven to be a valuable tool in the composite industry. It is highly useful in the preparation and design of an intelligent fabrication system for composite materials and also serves an integral function in the realization of such a system.

FDEMS in conjunction with other experimental techniques; such as Differential Scanning Calorimetry and Rheology, can provide an excellent characterization of a polymeric resin system. This includes the quantification of the interrelationship between macroscopic qualities, such as viscosity or degree of cure, and microscopic quantities, such as ionic mobility. Knowledge of these properties and their interdependence is essential to the successful and safe processing of polymer resins.

FDEMS, DSC and rheological techniques were combined in this investigation to provide successful correlations between viscosity, degree of cure and dielectric loss for the epoxy resin E905L. With this knowledge, an intelligent, closed-loop cure monitoring system for the fabrication of E905L/graphite composite parts by Resin Transfer Molding was designed.

Once the technique of successfully injecting the resin into the mold and achieving complete wet-out of the fiber preform was mastered, FDEMS was successfully employed to drive the RTM process. Software using in-situ, real-time FDEMS data controlled the fiber wet-out and intermediate hold of an E905L/graphite composite part. This closed-loop cure monitoring technique brought the part very close to a predetermined degree of cure and then terminated RTM the process.

VITA

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Philip John Kingsley was born in the small border town of Massena, New York on May 31, 1968. He graduated from Massena Central High School in June, 1986. Philip then attended the College of William and Mary in Virginia, where he received a B.S. with a concentration in Chemistry in May, 1990. He enrolled in the Chemistry Graduate program at William and Mary in June of 1990 and fulfilled the requirements for the program in December 1991.