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FORWARD

This final report covers the work performed from 1 August 1981 to 30 April 1983 under Contract N00019-81-C-0184 by the Material and Process Development Department of the McDonnell Aircraft Company, McDonnell Douglas Corporation, St. Louis, Missouri. The program was administered under the direction of the Naval Air Systems Command by Mr. Maxwell Stander and previously by Mr. Richard L. Dempsey.

The program was managed at McDonnell by Mr. R. J. Juergens, with Dr. J. F. Carpenter as Principal Investigator. Major contributors were Messrs. T. T. Bartels, G. T. Stillwell and C. E. Wilson of the McDonnell Materials Laboratory.

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MCDONNELL AIRCRAFT COMPANYLIST OF ABBREVIATIONS

RDS	Rheometrics Dynamic Spectrometer
CPS	Centipoise
HPLC	High Performance Liquid Chromatography
KCPS	Thousand Centipoise
GPC	Gel Permeation Chromatography
DSC	Differential Scanning Calorimetry
TADS	Thermal Analysis Data Station
phr	Parts per Hundred Resin
T	Temperature
T _{gel}	Temperature at Gel
T _{os}	Reaction Onset Temperature
T _{exo}	Reaction Exotherm Temperature
T _{CR}	Complete Reaction Temperature
η	Viscosity
η_0	Zero Time Viscosity
t	Time
T _{gel}	Time to Gel
G'	Storage Modulus
G''	Loss Modulus
ΔH	Enthalpy
ω	Dynamic Frequency
M	Torque
ϕ	Linear Heating Rate
k	Kinetic Factor

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MCDONNELL AIRCRAFT COMPANY**1.0 INTRODUCTION AND SUMMARY**

The processing parameters currently used in the fabrication of carbon/epoxy composite structures have essentially been derived from experience, as a result of extensive iterative testing. The purpose of this program was to develop a generic, and in-depth, scientific understanding of the effect of processing parameters on the behavior of prepreg resin.

Specifically the objectives of the program were to investigate the curing behavior of the neat resin under conditions relatable to the processing parameters of the companion carbon/epoxy prepreg material and to investigate the inter-relationships of volatiles transport, physiochemical and mechanical properties.

These objectives were accomplished by the development of a mathematical model for the rheology and complete cure of the 3501-6 resin system. The first part of the model is an expression which describes 3501-6 resin viscosity as a function of the time and temperature of cure. The model was used to compare the total flow behavior of the resin under varied conditions of cure and the behavior of three batches of resin in which the major epoxide component had different starting viscosities.

A computer program was written which uses the parameters of the mathematical model to plot viscosity profiles and calculate the total flow of 3501-6 resin for any desired combination of time and temperature of cure.

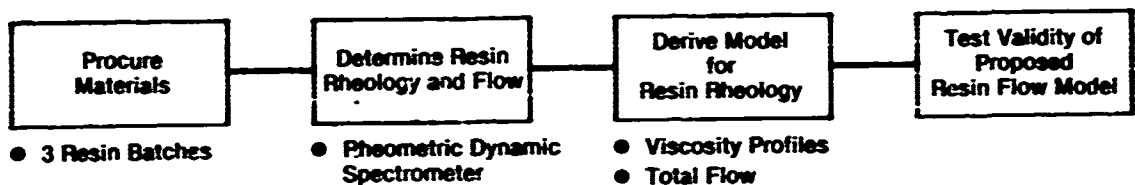
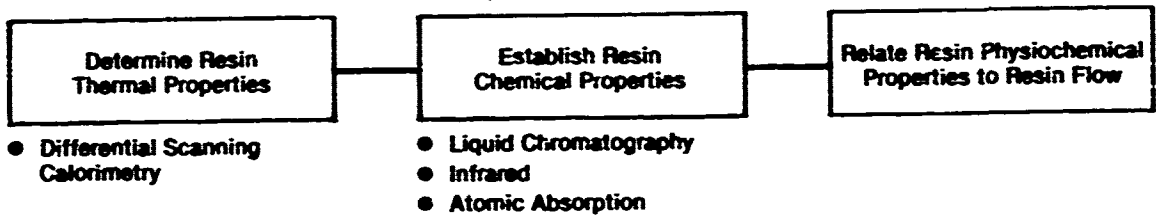
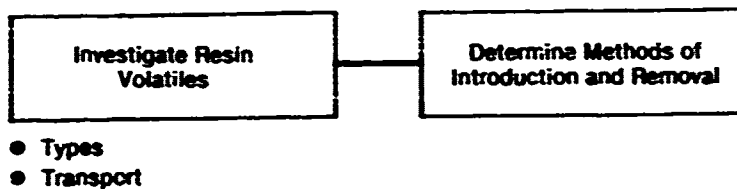
The mathematical model was expanded to include an expression for the time to complete cure as a function of cure temperature.

The model is applicable to other thermosetting resins and can be used to establish cure cycle conditions from a minimum of experimental determinations. It is also envisioned as being a useful methodology for the real-time control of automatic processing equipment (i.e. autoclave control).

Variations in the resin rheology of three special batches of resin were compared, as were differences in chemical composition of the prepreg and mechanical properties of the laminates. The effects of volatiles on resin processing were also investigated.

MCDONNELL AIRCRAFT COMPANY**2.0 PROGRAM PLAN**

The technical approach is given in the Program Plan, Figure 1. The rheology of 3501-6 resin was determined over a broad range of varied heating conditions. A model for the curing behavior of the neat resin was developed through the derivation of a mathematical expression which relates the resin viscosity to the time and temperature of resin cure. Physiochemical properties were determined and the thermal analysis data was used to expand the curing behavior model to include a mathematical expression which relates the time required for complete cure to temperature. A computer program was written which uses the parameters of the mathematical model to plot viscosity profiles for any desired cure cycle.

Phase I - Develop a Model for Resin Rheology and Flow**Phase II - Correlate Physiochemical Properties with Resin Rheology****Phase III - Determine Resin Volatiles Effects****Phase IV - Relate Resin and Laminate Properties****Figure 1. Program Plan**

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Three batches of 3501-6 resin were compared. These batches had been formulated to contain tetraglycidyl methylenedianiline (TGMDA) having three different starting viscosities. The types of resin volatiles and their transport mechanisms were investigated. As a last step, the resin properties determined in this program were compared with previously published data for their composite laminate properties.

PHASE I - DEVELOP A MODEL FOR RESIN RHEOLOGY AND FLOW

The objective of this phase was to develop a rheological model which represents the behavior of 3501-6 resin under conditions relatable to the processing parameters of the companion carbon/epoxide prepreg. This objective was accomplished by determining the rheological characteristics of the resin using the RDS-7700 rheometrics dynamic spectrometer. During resin heating the viscosity was measured for four different isothermal conditions, three dynamic heating conditions, and a typical cure cycle. A mathematical expression which relates the viscosity to the time of heating was written for each of the four isothermal conditions. The four equations were then used to derive a general expression which relates viscosity to the time and temperature of cure for all isothermal conditions.

It was found that the general expression for isothermal viscosity change could be converted to an expression applicable to dynamic heating (varied linear heating rates, by integrating the time dependent term. Then, together, the equations for isothermal and dynamic heating constitute a set of equations which predicts the viscosity for any time/temperature sequence of resin cure.

This set of equations is proposed as a mathematical model for resin rheology during cure. A computer/plotter was programmed to include the equations of the model, and viscosity profiles are automatically produced for any combination of cure cycle parameters.

The rheologies of three batches of 3501-6 resins were compared. These batches were made by standard processing and with normal component concentrations, but contained TGMDA with varied starting viscosities.

PHASE II - CORRELATE PHYSIOCHEMICAL PROPERTIES WITH RESIN RHEOLOGY

The objective of this phase was to determine relationships between physiochemical properties and resin rheology and to determine the applicability of physiochemical data to an expanded curing behavior model. Differential scanning calorimetry (DSC) was used for thermal analysis of the resin system and the chemical characteristics were determined using infrared, liquid chromatography and atomic absorption. The physiochemical properties were compared with the variations in rheology for the three resin batches tested.

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The DSC data was used to expand the model for resin curing behavior to include a mathematical expression which relates temperature to the time required for complete cure.

PHASE III - DETERMINE RESIN VOLATILES EFFECTS

The objective of this phase was to characterize resin volatiles and explore techniques useful to modeling their formation and migration during cure. As-received resins were initially compared under ambient pressure cure and vacuum cure conditions for the types and amounts of volatiles. Bubble size and distribution was compared using a Bausch and Lomb image analyzer. Later, prepreg materials were compared for outgassing characteristics by submerging the specimens in silicone oil and observing bubble formation during resin cure.

A means was developed to introduce known amounts of both condensible and non-condensable volatiles using a method that is applicable to the study of resin volatiles transport in neat resin and the characterization of voids in cured composites.

PHASE IV - RELATE RESIN AND LAMINATE PROPERTIES

The objective of this phase was to determine whether the neat resin properties determined in this program exhibited any correlation with previously determined laminate properties. The objectives were achieved by comparing laminate physical and mechanical properties, determined earlier in Reference (1), with the rheological and physiochemical properties determined in this program. The resin batches compared differed only in the viscosity of the base epoxide (TGMDA) used in their formulation.

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MCDONNELL AIRCRAFT COMPANY**3.0 TECHNICAL RESULTS AND DISCUSSION**

Three batches of 3501-6 resin were selected for the program. The differences among the three batches of resin is in the starting viscosity of the major epoxide component, tetraglycidyl methylenedianiline (TGMDA):

<u>BATCH</u>	<u>TGMDA VISCOSITY (CPS)</u>
B-1	10,700
B-2	14,000
B-3	18,000

All batches were formulated by the supplier's standard processing procedure and all were formulated to contain the following standard concentrations of starting components:

<u>COMPONENT</u>	<u>TOTAL PERCENT (WT)</u>
Tetraglycidyl Methylenedianiline	56.5
Alicyclic Diepoxy Carboxylate	9.0
Epoxy Cresol Novalac	8.5
4,4' Diaminodiphenyl Sulfone	25.0
Boron Trifluoride Amine Complex	1.1

In earlier work, these batches gave different behavioral response to processing, Reference (1).

3.1 PHASE I - DEVELOP A MODEL FOR RESIN RHEOLOGY AND FLOW - In this phase resin flow measurements were made under varied cure modes and a mathematical model was developed which describes 3501-6 resin viscosity and flow as a function of the time and temperature of processing. The effects of varied cure cycles on resin flow was demonstrated. The model was used to compare the rheologies of three batches of resin having varied starting viscosities for the major epoxide component. The flow properties of the three batches were shown to be quite similar.

Instrumental Technique - The Rheometrics RDS-7700 instrument was used for this program. It is a dynamic, oscillatory rheometer capable of measurements over a wide range of temperatures. It can be programmed for any combination of linear heating rates, isothermal holds, and simulated cure cycle conditions. It provides continuous printout and data plots for selected properties, including dynamic viscosity (η), loss modulus (G'') and storage modulus (G'), together with time (t), temperature (T), and torque (M).

The rheological properties for the neat resins were measured under the following conditions:

Starting Temperature	= 50°C
Strain	= 50%
Shear Rate	= 10 rads/sec
Plate Gap	= 0.5mm $\pm$ 0.01mm

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All samples were preconditioned at room temperature by pressing about 1 gram of resin between two pieces of non-porous Teflon cloth (CHR-6TB) to produce a resin wafer about 5mm thick. The wafers were exposed in a vacuum desiccator for 24 hr and removed just prior to running the rheograms. The sample preconditioning was used to remove moisture and any other volatiles that might cause erratic variations in rheology.

The RDS-7700 instrument was used to generate plots of viscosity vs. time for the temperature conditions of the tests. These viscosity profile data were used to calculate a measure of the total flow achieved for the varied time/temperature parameters of the tests.

The reciprocal of viscosity is termed "fluidity". Fluidity integrated as a function of time was taken as a measure of total flow under the pressure conditions of the rheometrics instrument.

Isothermal Heating Conditions - The change in viscosity as a function of time and temperature was first studied for the isothermal case.

Under isothermal conditions the change in viscosity with time can be expressed by the equation:

$$\log \eta = k(t) + \log \eta_0 \quad (1)$$

where: η = Time Dependent Viscosity (poise)
 η_0 = Zero Time Viscosity (Constant for Isothermal Runs)
 k = Kinetic Factor
 t = Time (minutes)

This model for the isothermal case has been proposed by several investigators, References (2-6). Figure 2 shows a plot of four isothermal runs for viscosity as a function of time at 135°C. A linear regression line for $\log \eta$ vs. time is also shown. The minimum viscosity was reached in an average time of 6 minutes.

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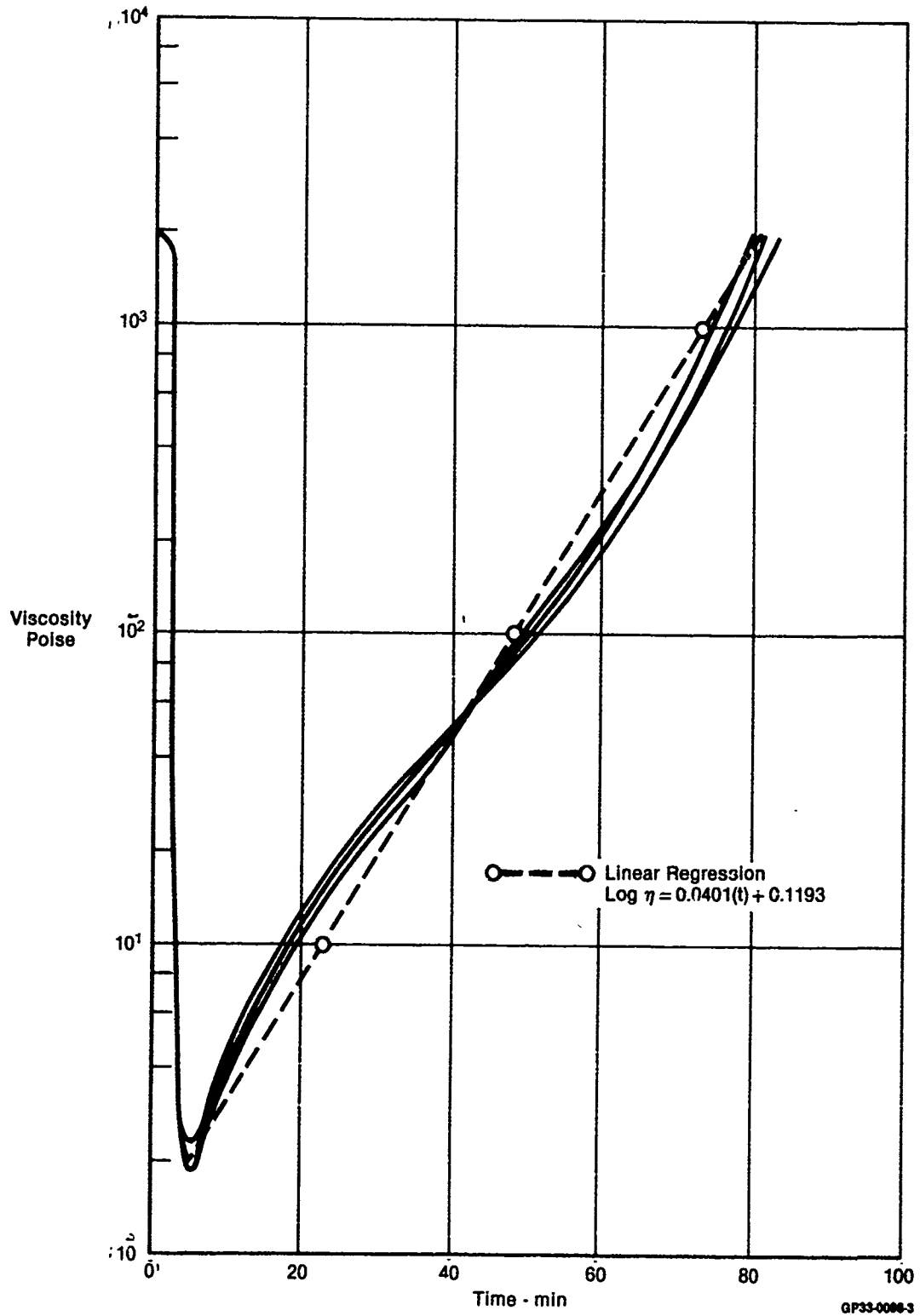


Figure 2. Isothermal Rheograms in Replicate for 3501-6 Resin, Batch B-1 @ 135°C

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Replicate runs were made for Batch B-1 at four different temperatures. The values calculated for the constants k and $\log \eta_0$ at each temperature are given in Table 1. The kinetic factor (k) decreases with decreasing temperature and zero-time viscosity (η_0) increases with decreasing temperature.

Table 1. Constants for Isothermal Viscosity Equation, Batch B-1
 $[\log \eta = k(t) + \log \eta_0]$

Temperature (°C)	k	$\log \eta_0$	Correl Coef (r^2)
140	0.0554	-0.0517	0.982
135	0.0401	0.1193	0.985
130	0.0318	0.2856	0.988
125	0.0247	0.4001	0.988

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The kinetic factor (k) can be expressed as a function of temperature (T , °K) by an expression similar to that derived in Reference (7).

$$k = \frac{C_1 10^{A_1/T}}{T^2} \quad (2)$$

For Batch B-1, $\log (kT^2)$ vs. $1/T$ is solved by linear regression to give:

$$\log (kT^2) = - \frac{4140.2}{T} + 13.9885 \quad (3)$$

$$r^2 = 0.994 \text{ (correlation coef.)}$$

Thus:

$$k = 9.74 \times 10^{13} \left[\frac{10}{T^2}^{-4140/T} \right] \quad (4)$$

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In a like manner, the isothermal values for $\log \eta_0$ (Equation 1) for Batch B-1 was reduced by assuming:

$$\eta_0 = \frac{C_2 10^{A_2/T}}{T^2} \quad (5)$$

The linear regression of $\log (\eta_0 T^2)$ vs. $1/T$ gave the values of the constants as:

$$\begin{aligned} C_2 &= 8.81 \times 10^{-7} \\ A_2 &= 4645.8 \end{aligned} \quad (6)$$

with a correlation coefficient of $r^2 = 0.989$.

Thus, a mathematical model for isothermal resin flow is given by the following expression, which relates viscosity to the time and temperature of processing:

$$\log \eta = C_1 \left[\frac{10^{A_1/T}}{T^2} \right] (t) + \log \left[C_2 \frac{10^{A_2/T}}{T^2} \right] \quad (7)$$

For Batch B-1 the expression is:

$$\log \eta = 9.74 \times 10^{13} \left[\frac{10^{-4140.2/T}}{T^2} \right] (t) + \log \left[8.81 \times 10^{-7} \times \frac{10^{4646/T}}{T^2} \right] \quad (8)$$

A desktop computer, interfaced with a digital X-Y plotter, was programmed to solve Equation (7) and automatically plot viscosity as a function of time/temperature.

A computer generated plot for the isothermal viscosity profile of Batch B-1, at 135°C, is shown in Figure 3. The computer program provides for the superimposition of experimental data. Each point shown on the rheogram in Figure 3 represents an average viscosity value for replicate determinations. Figure 4 shows a computer drawn family of curves for isothermal determinations at 125, 130, 135, and 140°C.

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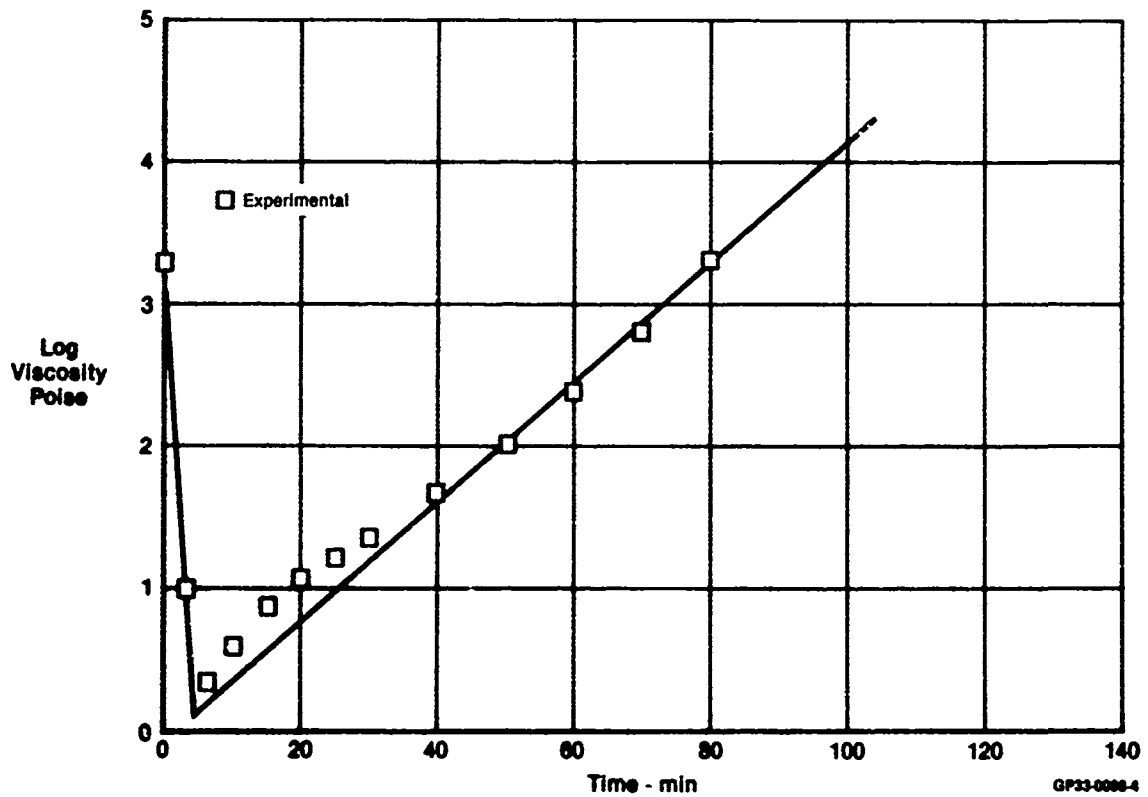


Figure 3. Computer Drawn Isothermal Rheogram for 3501-6 Resin, Batch B-1 @ 135°C

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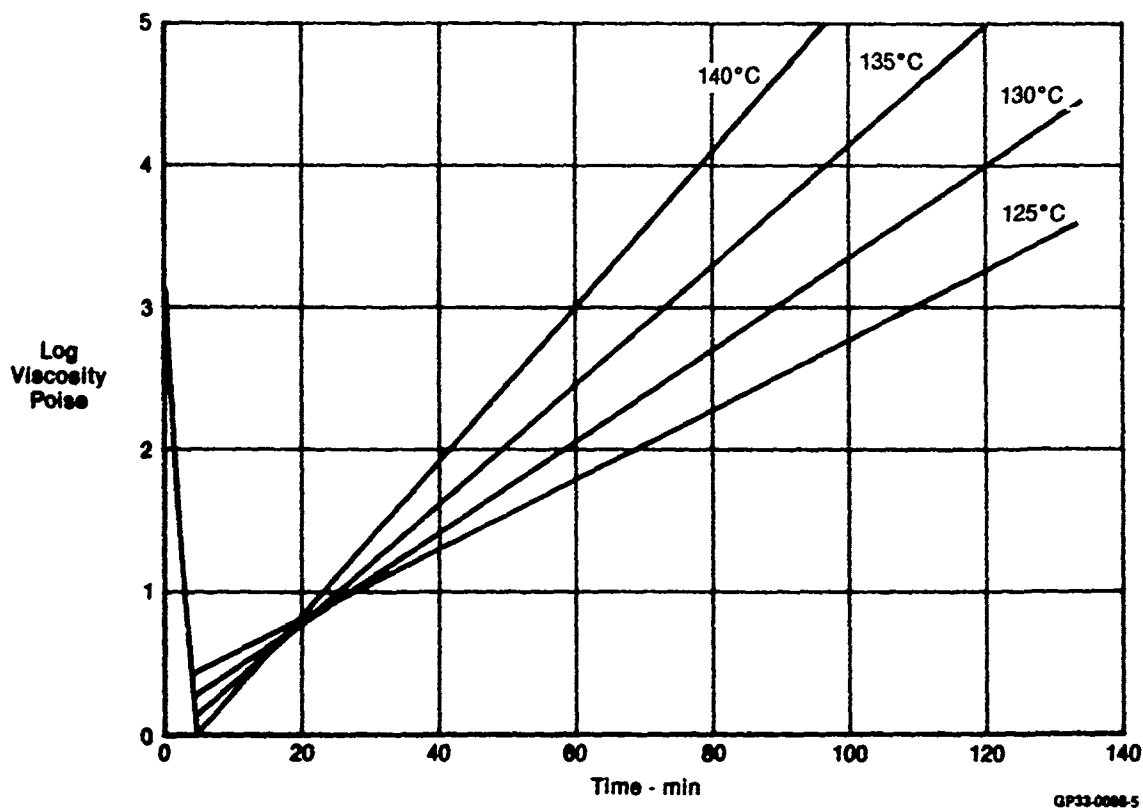


Figure 4. Computer Drawn Family of Isothermal Rheograms for 3501-6 Resin, Batch B-1 @ 125, 130, 135 and 140°C

Dynamic Heating Conditions - Dynamic runs were made for the three test batches of 3501-6 at linear heating rates of 1, 2, and 4°C/min. Typical rheograms for Batch B-1 at the three different heating rates are shown in Figure 5. Data for critical points (minimum viscosity and gel) of the curves for Batches B-1, B-2, and B-3 are given in Table 2. As expected, the faster the heat-up rate, the lower the minimum viscosity and the shorter the time to gel.

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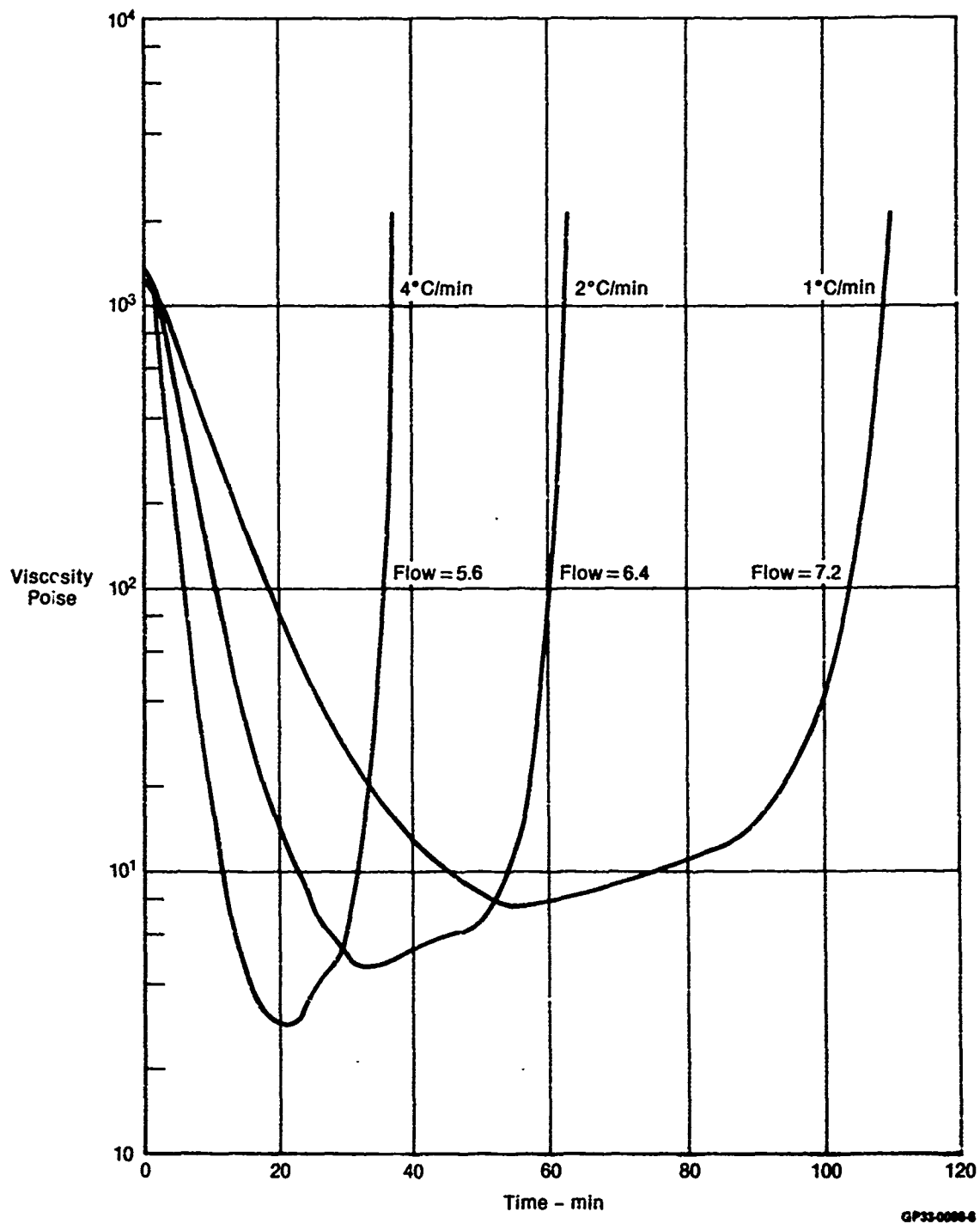


Figure 5. Rheograms for 3501-6 Batch, B-1 for Different Heating Rates

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Table 2. Rheometric's Data for Varied Linear Heating Rates

Batch Number	Heating Rate, ϕ ($^{\circ}\text{C}/\text{min}$)	Minimum Viscosity, η (Poise)	Temperature, T ($^{\circ}\text{C}$) at Minimum η	Time to Gel*, t_{gel} (min)	Temperature at Gel Point, T_{gel} ($^{\circ}\text{C}$)
B-1	1	7.2	110	111	167
	2	4.7	120	63	184
	4	2.7	130	36	194
B-2	1	6.8	112	115	171
	2	5.7	126	63	186
	4	3.2	136	36	202
B-3	1	8.6	114	112	168
	2	5.8	122	64	186
	4	3.2	140	36	206

*1,000 poise

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The temperatures for minimum viscosity and gel can be predicted for other linear heating rates by the equations given in Table 3. Calculation of these temperatures provides useful information; however, what is needed is a means of using the data obtained from a minimum number of isothermal runs to predict the viscosity profiles obtained under the dynamic conditions of varied linear heating rates.

Table 3. Correlation of Linear Heating Rate Data

Batch Number	Equation Relating Temperature and Heating Rate for Minimum Viscosity	Equation Relating Temperature and Heating Rate for Resin Gel*
B-1	$\log \phi = -\frac{4,535}{T(^{\circ}\text{K})} + 11.8465$ $r^2 = 0.999$	$\log \phi = -\frac{4,451}{T(^{\circ}\text{K})} + 10.0977$ $r^2 = 0.982$
B-2	$\log \phi = -\frac{3,900.2}{T(^{\circ}\text{K})} + 10.1149$ $r^2 = 0.987$	$\log \phi = -\frac{4,095.9}{T(^{\circ}\text{K})} + 9.2256$ $r^2 = 0.999$
B-3	$\log \phi = -\frac{3,550.6}{T(^{\circ}\text{K})} + 9.2212$ $r^2 = 0.959$	$\log \phi = -\frac{3,346.7}{T(^{\circ}\text{K})} + 7.5900$ $r^2 = 1.000$

 ϕ = Heating rate ($^{\circ}\text{K}/\text{min}$)

*1,000 poise

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Equation (1) can be converted into a form applicable to the dynamic heating case by replacing the first (isothermal) term with an integral expression to give:

$$\log \eta = \int_{t_0}^{t_{gel}} k \, dt + \log \eta_0 \quad (9)$$

For linear heating rates, time can be expressed in terms of temperature by:

$$t = \frac{T - T_0}{\phi} \quad \text{and} \quad dt = \frac{dT}{\phi} \quad (10)$$

Equation (7) is then modified to give the following mathematical model for dynamic heating:

$$\log \eta = C_1 \int_{T_0}^{T_{gel}} \left[\frac{10^{A_1/T}}{\phi T^2} \right] dT + \log \left[\frac{C_2 10^{A_2/T}}{T^2} \right] \quad (11)$$

The computer/plotter was programmed to include Equation (11). A computer plot for dynamic heating at 1°C/min, together with experimental points, is shown in Figure 6.

Equation (7) for isothermal heating, together with Equation (11) for the dynamic heating case, constitute a mathematical model which provides the capability to calculate viscosity for any time/temperature sequence (i.e., the resin rheology portion of a processing model).

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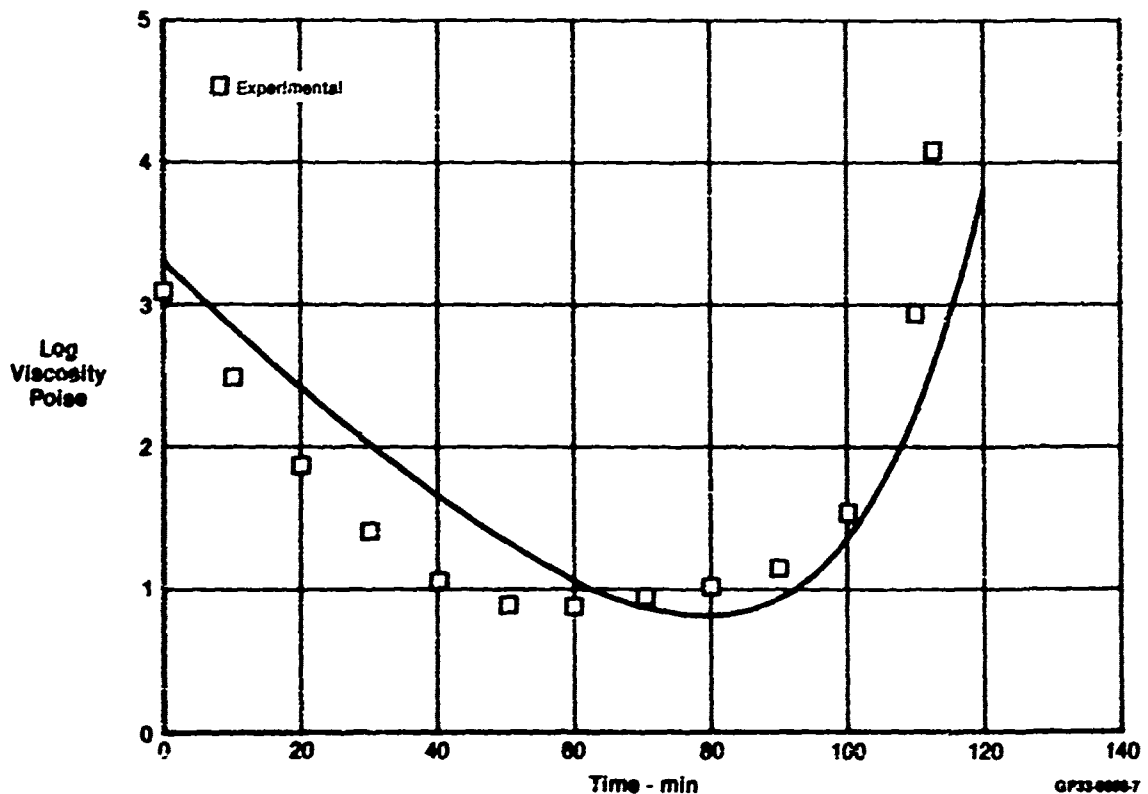
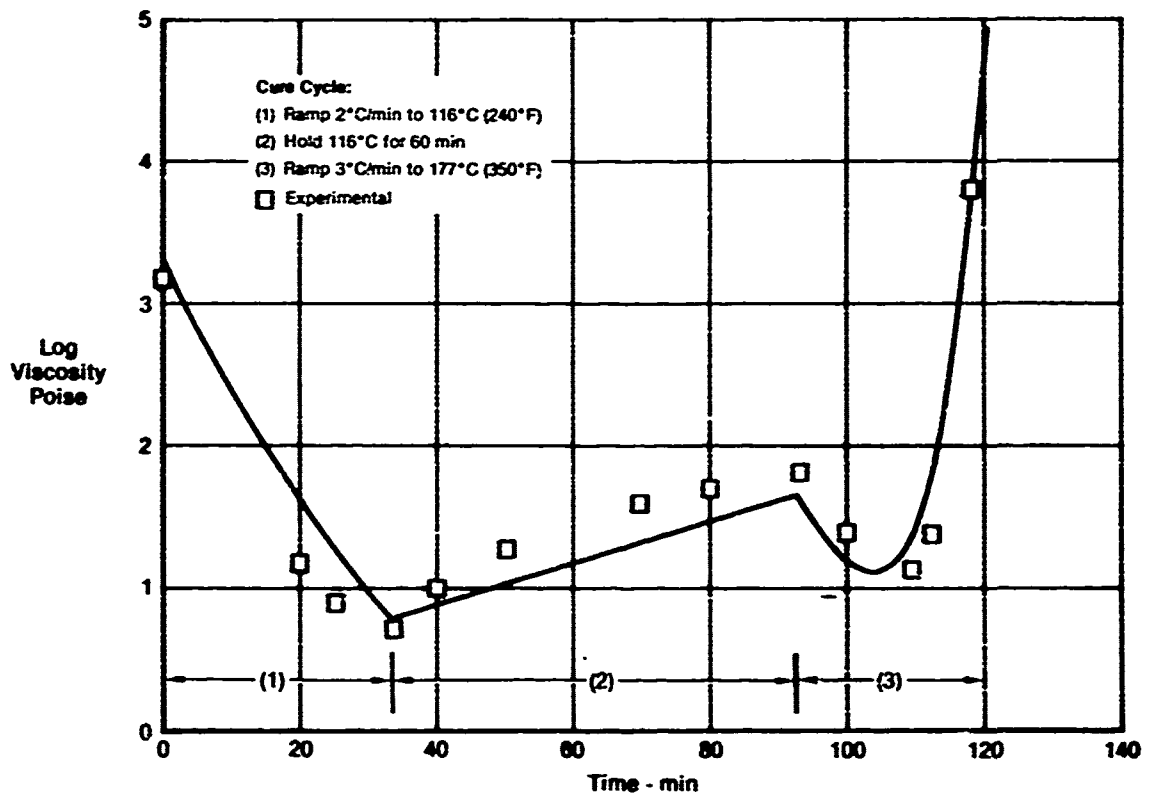


Figure 6. Computer Drawn Dynamic Heating Rheogram for 3501-6, Batch B-1 @ 1°C/min

To verify the suitability of the model, a typical cure cycle run was made on the Rheometrics instrument. The cycle included a ramp at 2°C/min to 116°C, a hold at 116°C for 60 minutes, a ramp at 3°C/min to 117°C, followed by a hold at 177°C. Figure 7 shows experimental data together with a computer drawn curve using the rheology model.

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Figure 7. Computer Drawn Cure Cycle Rheogram for 3501-S, Batch: B-1

Isothermal viscosity was determined for Batches B-2 and B-3. As with Batch B-1, the runs were made in replicate at 125, 130, 135, and 140°C. The mathematic model for each batch was derived from these data. The parameters for the model for each of the three batches is given in Table 4.

Table 4. Batch Parameters for Mathematical Model

$$\log \eta = C_1 [10^{A_1 t / T^2}] (t) + \log [C_2 10^{A_2 / T^2}]$$

Batch	C_1	A_1	C_2	A_2
B-1	9.74×10^{13}	-4,140.2	8.81×10^{-7}	4,645.8
B-2	1.08×10^{12}	-3,331.1	1.31×10^{-5}	4,144.7
B-3	2.16×10^{12}	-3,467.1	1.45×10^{-5}	4,140.8

Where: η = Viscosity (Poise) t = Time (min) T = Temperature (°K)

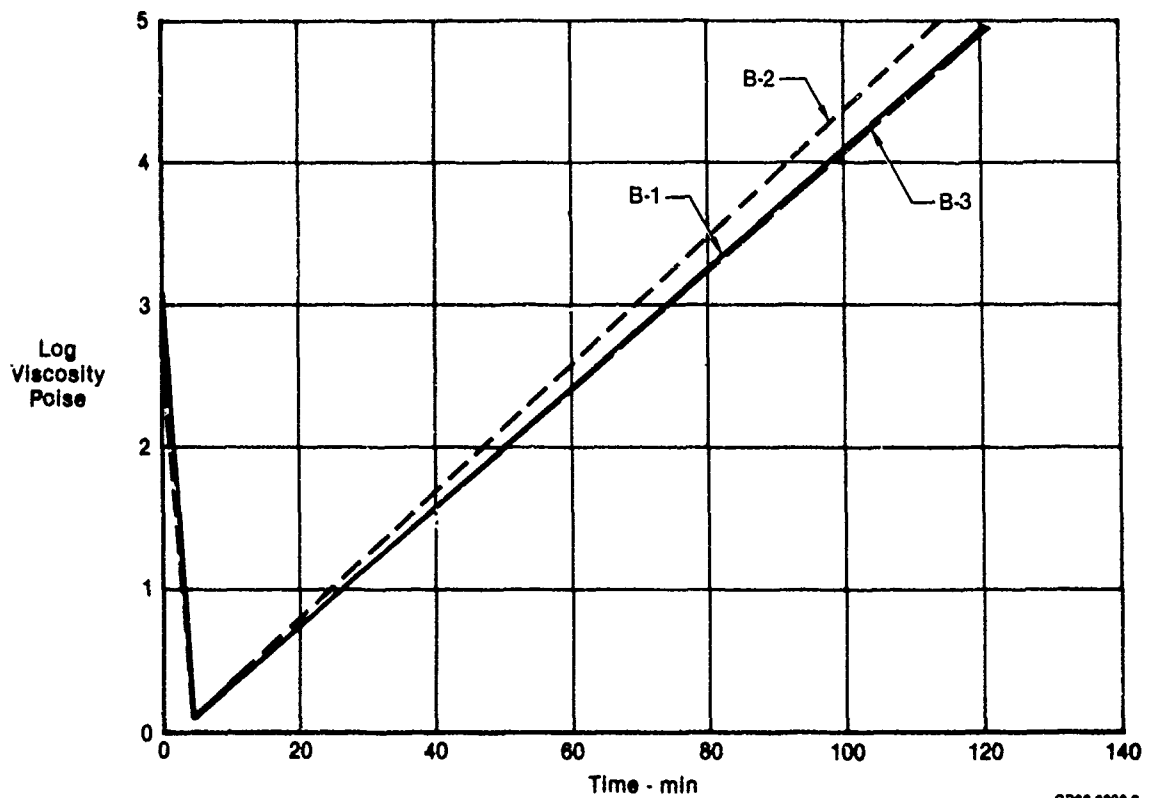
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The rheology models for the three batches were used to generate computer curves depicting the viscosity profiles.

The rheological properties of Batches B-1, B-2, B-3 were compared using computer drawn curves. The isothermal viscosity profiles are shown in Figure 8. Figure 9 shows batch comparison at a heating rate of 1°C/min and Figure 10 shows the model rheograms under the conditions of a typical cure cycle. The viscosity profiles for the three resin batches are quite similar and show no significant trends relatable to the viscosity of the TGMDA used in their formulation.



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Figure 8. Computer Drawn Isothermal Rheograms for 3501-6 Resin Comparing Batches B-1, B-2, and B-3 @ 135°C

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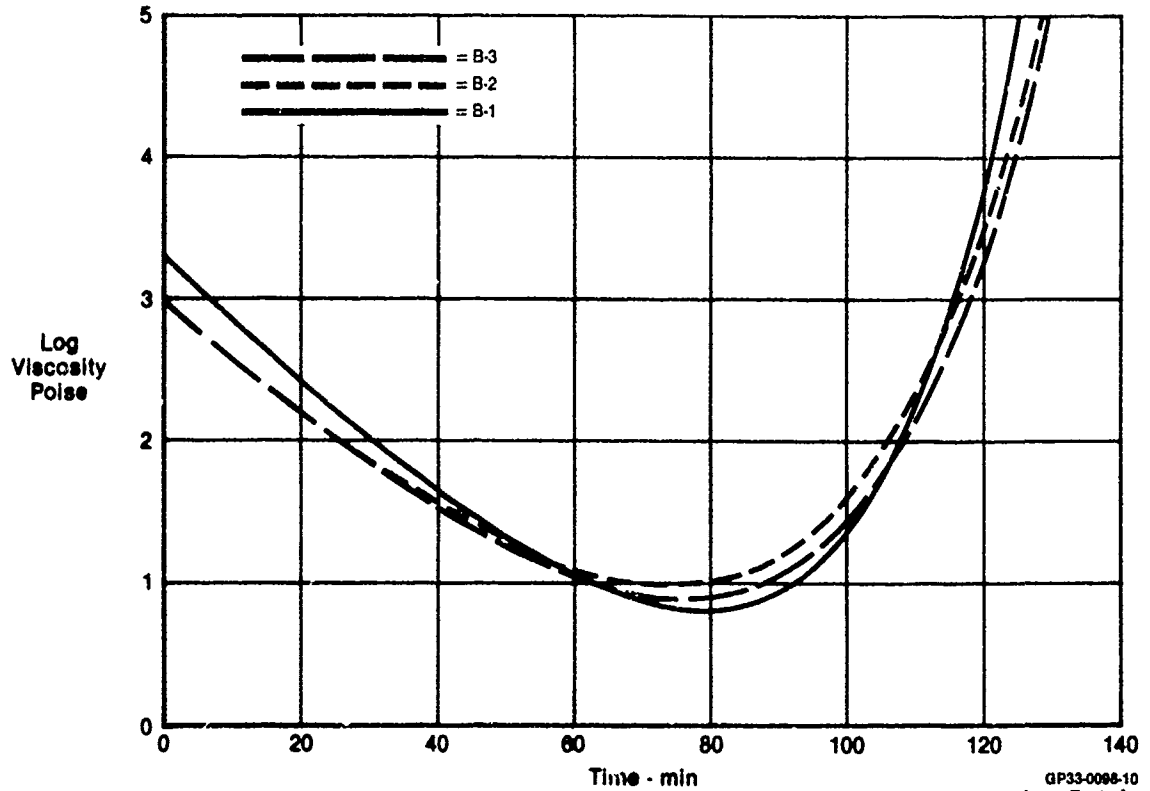


Figure 9. Computer Drawn Dynamic Heating Rheograms for 3501-6 Resin Comparing Batches B-1, B-2, and B-3 @ 1°C/min

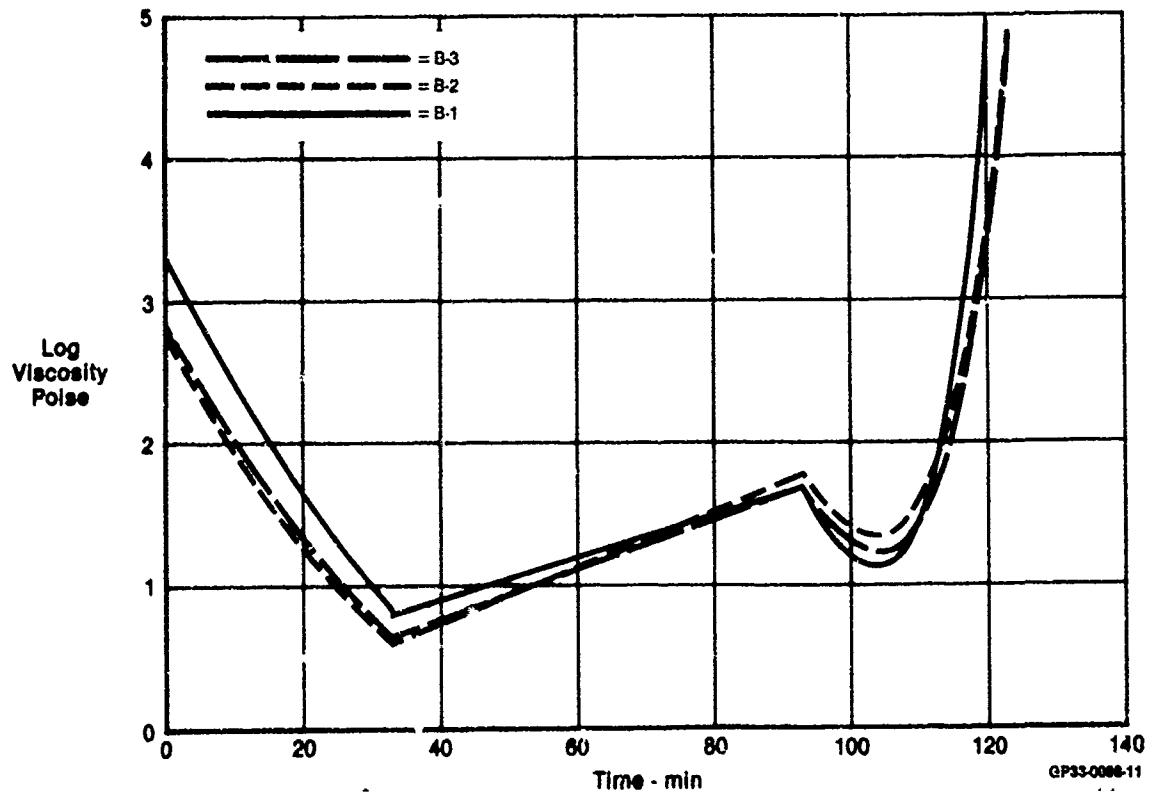


Figure 10. Computer Drawn Cure Cycle Rheograms for 3501-6 Resin Comparing Batches B-1, B-2, and B-3

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Total Resin Flow - The total flow at constant pressure is described as the value obtained by integrating the reciprocal of viscosity (fluidity) from zero-time (t_0) to the point where the flow ceases, i.e., time to gel (t_{gel}):

$$\text{FLOW NUMBER} = \int_{t_0}^{t_{gel}} \frac{dt}{\eta} \quad (12)$$

Flow numbers for Batches B-1, B-2, and B-3 are shown in Table 5. Individual values obtained in replicate runs are shown in parentheses. These values were obtained by machine-integration of the viscosity profiles from the RDS experimental runs and not from the rheology model. The flow-numbers are a measure of total flow for each condition of time and temperature under an equivalent pressure.

Table 5. Flow Numbers for 3501-6 Neat Resin Batches

		Flow Numbers (Minutes/Poise)		
Cure Mode	Batch	B-1	B-2	B-3
1. Dynamic (°C/min)				
	1	7.24 (6.89, 7.59)	7.51 (8.43, 6.58)	6.16 (5.93, 6.40)
	2	6.43 (6.42, 6.44)	5.52 (5.52, 5.53)	5.55 (5.26, 5.85)
	4	5.61 (5.36, 5.86)	5.05 (4.91, 5.19)	4.19 (4.61, 5.76)
2. Isothermal (°C)				
	125	5.71 (5.63, 5.66, 5.85)	5.38 (5.13, 5.63)	6.04 (5.69, 6.39)
	130	5.55 (5.46, 5.63)	4.53 (4.46, 4.59)	5.30 (4.67, 5.93)
	135	5.08 (4.86, 5.00, 5.02, 5.40)	4.25 (4.25, —)	4.46 (4.22, 4.71)
	140	4.91 (4.36, 5.45)	4.29 (4.35, 4.22)	4.33 (3.98, 4.09, 4.91)
3. Cure Cycle		5.96 (6.14, 5.77)	—	—

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For the three batches tested, the following observations were made:

- o Dynamic Cure Mode - Increasing the heating rate gives lower total flow. The total flow of a resin batch is in line with the viscosity of the starting TGMDA.
- o Isothermal Cure Mode - Increasing the isothermal temperature also gives lower total flow. The total flow of Batch B-3 is higher than expected from the relative viscosity of the starting material.
- o Cure Cycle - The cure cycle tested (Ramp at 2°C/min to 116°C - hold 116°C for 60 min - ramp 3°C/min to gel) did not maximize flow.
- o The data indicates that it is possible to achieve equivalent flow for all batches by tailoring cure conditions. These batches represent variation in TGMDA viscosity over the full range of commercially available material.

Flow numbers can be calculated directly from the viscosity curves generated by the rheology model. The calculated values are in general agreement with those obtained by direct measurement of the individual experimental rheograms; however, they are not considered to be as accurate. To improve the accuracy of the calculated flow numbers it will be necessary to assume a higher order regression fit than the linear regression assumed for equation 7.

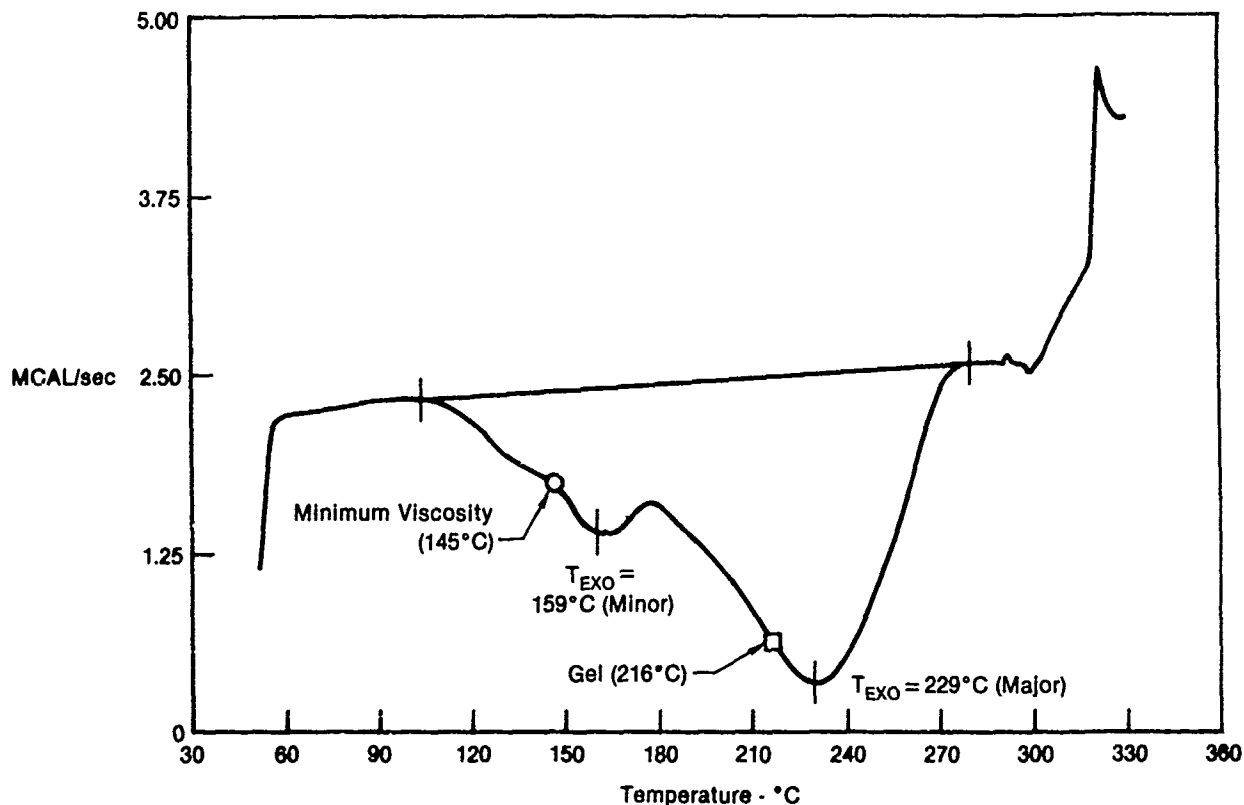
3.2 PHASE II - CORRELATE PHYSICOCHEMICAL PROPERTIES WITH RESIN RHEOLOGY - The Objective of this phase was to determine inter-relationships for physiochemical properties and the rheology of the resin batches studied and to determine whether physiochemical data can be used to expand the processing model. The thermal analysis data was shown to be applicable to the development of a mathematical expression for calculating the time to complete cure from the cure temperature. This thermokinetic model, together with the rheology model constitute a viscokinetic model for resin curing behavior.

Determine Resin Thermal Properties - Thermal analysis of the 3501-6 resin system was performed by differential scanning calorimetry using the Perkin Elmer DSC-2 instrument.

A typical DSC thermogram is shown in Figure 11. The initial minor exotherm is associated with the BF₃ catalyst and may be due to the dissociation of the BF₃ - amine complex together with the reaction of the novalac epoxide with the sulfone (DDS) curing agent. The major exotherm is mainly due to the TGMDA and carbonyl epoxides reacting with the remaining curing agent. The DSC instrument prints out the exotherm peak temperatures. The points for minimum viscosity and gel, as determined by RDS, are shown on the thermogram to locate these events relative to the exothermal cure reaction.

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Figure 11. DSC Thermogram for 3501-6 Resin, Batch B-1 @ 10°C/min

The DSC exotherm peak temperatures are compared with the RDS viscosity temperatures (minimum viscosity and gel point) in Table 6. There appears to be no well defined quantitative correlations between these data. A very general observation for the varied linear heating rates is that minimum viscosity is near the minor DSC exotherm peak and the gel point is near the major DSC exotherm peak. The reaction associated with the minor exotherm causes the viscosity to start increasing and the flow is decreased compared with some other epoxide composite matrix systems, which do not contain BF_3 , such as Narmco 5208, Fiberite 976 and Hercules 3502.

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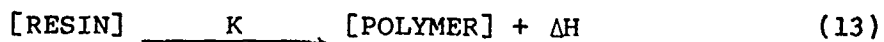
MCDONNELL AIRCRAFT COMPANY**Table 6. Comparison of Event Temperatures for Viscosity (RDS) and Thermal (DSC) Data for Linear Heating Rates**

Heating Rate (°C/min)	Batch Number	Temperature (°C)			
		RDS (Minimum Viscosity Point)	DSC (Minor Peak Exotherm)	RDS (Gel Point)	DSC (Major Peak Exotherm)
2.5	B-1	123	120	186	196
	B-2	128	116	191	196
	B-3	129	120	192	196
5.0	B-1	133	148	200	215
	B-2	141	145	207	213
	B-3	144	145	213	211
10.0	B-1	145	159	216	229
	B-2	155	155	225	228
	B-3	159	158	235	229
20.0	B-1	157	172	233	249
	B-2	170	172	244	248
	B-3	175	172	259	248

GP33-0098-20

To study the kinetics of the 3501-6 cure reaction the Perkin Elmer DSC-2 was interfaced with a thermal analysis data station (TADS) for acquisition and manipulation of data.

Kinetics of 3501-6 Cure Using DSC-2 Data and the TADS Program - The exothermal cure reaction for transformation of the B-staged starting resin to the cured matrix polymer may be expressed as:

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Based on the decrease of resin concentration with time, the rate equation can be written as:

$$\frac{d\alpha}{dt} = K (1 - \alpha)^n \quad (14)$$

Where:

α = degree of polymerization
 t = time
 K = rate constant
 n = parameter for data fit

The reaction expressed in Equation (13) is assumed to be diffusion controlled, in which case the order of the reaction is meaningless. Therefore, the term n is a parameter for mathematical data fit and is not applicable to defining the true reaction mechanism.

The classical Arrhenius equation can be used to express the rate constant (K) as a function of the temperature (T):

$$K = K_0 \exp (-E/RT) \quad (15)$$

Where:

R = gas constant
 T = temperature ($^{\circ}K$)
 E = activation energy
 K_0 = constant

Combining equations (14) and (15) gives the kinetic expression:

$$\frac{d\alpha}{dt} = K_0 \exp (-E/RT) (1-\alpha)^n \quad (16)$$

R. Rush, Reference (8) and R. Fyans, Reference (9) have described the use of Model DSC-2 equipped with the thermal analysis data station (TADS) and the TADS kinetic software package for data manipulation in solving equation (16).

It is assumed that E and n are independent of $(1-\alpha)$ and are dependent of the DSC scan rate. These independent relationships were shown for a solid diffusion controlled reaction by Crane, Dynes and Kaelble, Reference (10). The degree of polymerization α , can be expressed in many ways. The simple approach is used here.

In order to calculate α , the partial areas of the exotherm must be obtained. This is done by a subroutine in TADS which determines the total ΔH and partial areas by using Simpson's Rule for the area under the DSC curve.

$$\alpha = \frac{\Delta H \text{ partial}}{\Delta H \text{ total}} \quad (17)$$

$1 - \alpha$ is then calculated and becomes a known for the solving of Equation (16).

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Equation (16) can be reduced to a linear form by taking the natural logarithm to obtain:

$$\ln \frac{d\alpha}{dt} = \ln K_0 - (E/RT) + n \ln (1 - \alpha) \quad (18)$$

Equation (18) has DSC knowns of $\ln \frac{d\alpha}{dt}$, $1/T$ and $(1 - \alpha)$ as variables to solve for K_0 , E and n . This is done by multi-linear regression in TADS.

The kinetic factors calculated for 3501-6 neat resin Batch B-1 are given in Table 7. The data indicate a pseudo first order reaction. The magnitude of the activation energy indicates a diffusion controlled network extension of epoxide/hardener system.

Table 7. DSC-2 Kinetic Factors for 3501-6 Resin Batch B-1

Heating Rate Kinetic Factor	1.25 (°C/min)	2.5 (°C/min)	5.0 (°C/min)
Constant, $\ln K_0$ (sec ⁻¹)	15.4	13.4	10.5
Activation Energy, E_a (cal/g)	19.8	18.2	15.6
Pseudo Reaction Order (n)	1.2	1.5	0.9

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The 3501-6 resin has a bimodal cure exotherm. The set of kinetic factors reported here is for the major exotherm. A similar set of data was determined for the preliminary minor exotherm that is due to the $B\bar{F}_3$ catalyst. The minor exotherm data was not consistent and reflects a limitation that has not been resolved.

DSC Data and a Thermokinetic Model for Complete Cure - The kinetic factors calculated using the TADS software program gave data that may be used for reference and in comparing 3501-6 with other thermosetting resins. However, the form of the kinetics equation provided by TADS is not immediately applicable to a processing model.

An approach that will allow the use of DSC to predict the time/temperature combinations required for complete cure has been reported by Carpenter, Reference (7).

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This technique uses the temperature for complete reaction (T_{CR}), shown in Figures 12-14. A plot of $\log \phi$ vs $1/T_{CR}$ for three different heat up rates gives the following equation:

$$\log \phi = - \frac{4875}{T_{CR}} + 9.821 \quad (19)$$

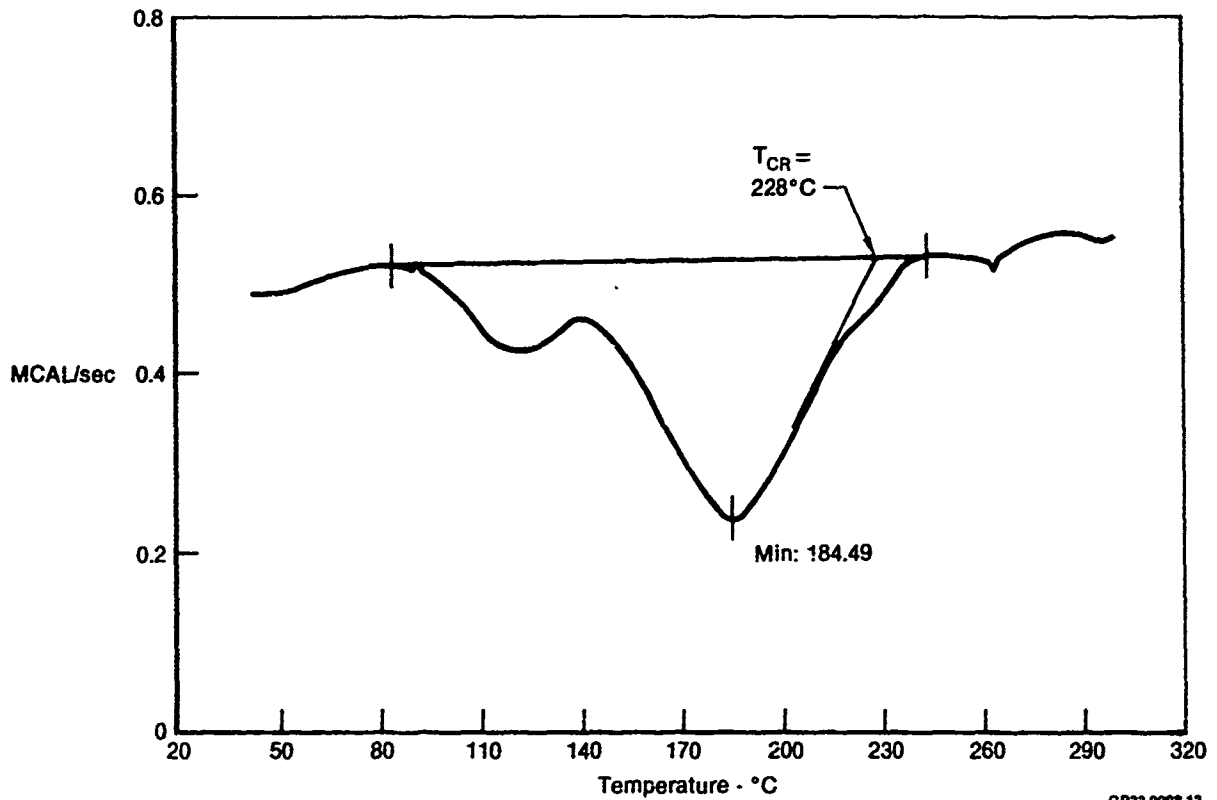


Figure 12. DSC Thermogram for 3501-6, Batch B-1, @ 1.25°C/min

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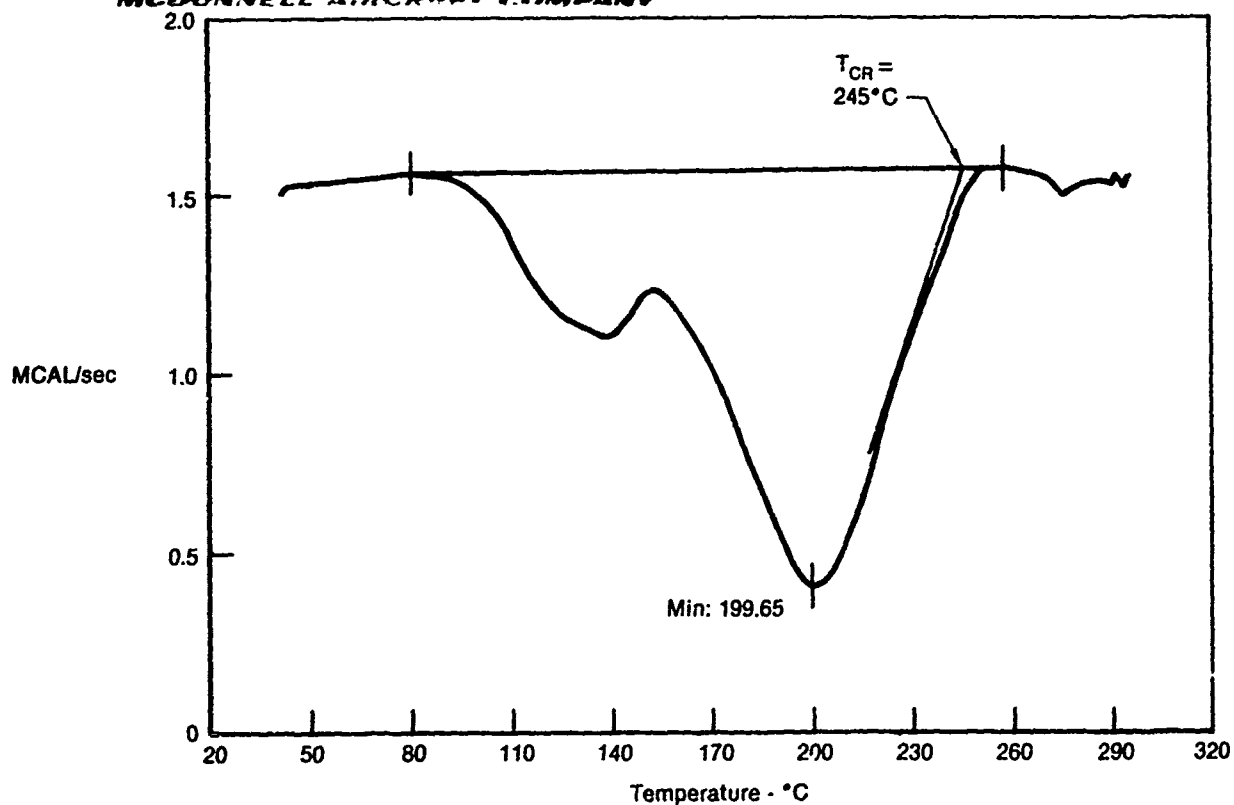


Figure 13. DSC Thermogram for 3501-6, Batch B-1, @ 2.5°C/min

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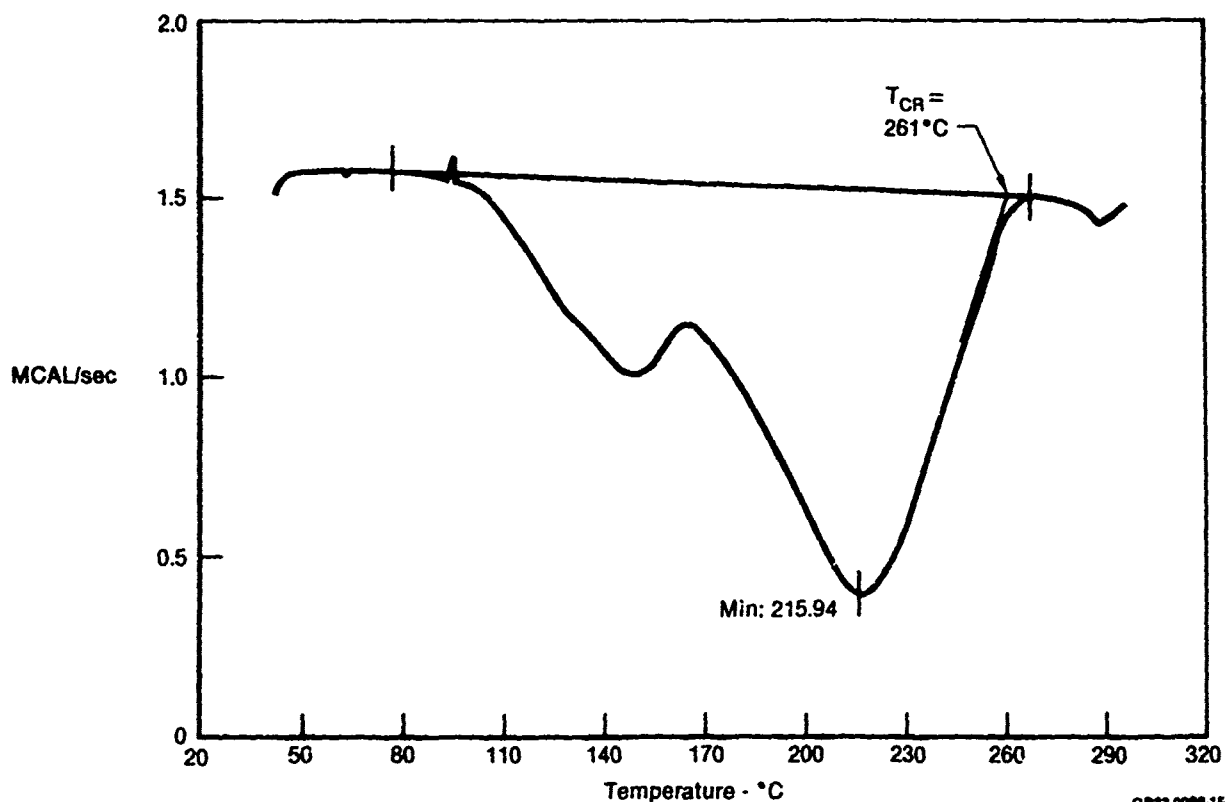


Figure 14. DSC Thermogram for 3501-6, Batch B-1, @ 5°C/min

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The data is given in Table 8.

Table 8. Thermal Data for Complete Cure of 3501-6, Batch B-1

Critical Point	Heating Rate, ϕ (°C/min)	Temperature (°C)	Equation
Temperature for Complete Reaction (T_{CR})	1.25	228	$\log \phi = -\frac{4,875}{T} + 9.821$
	2.50	245	$r^2 = 0.9987$
	5.00	261	

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As was shown in Reference (7), the isothermal time to complete reaction (t_{CR}) can be expressed as a function of cure temperature by the following equation:

$$t_{CR} = c T^2 10^{4875/T} \quad (20)$$

The constant, (c), can then be determined from:

$$c = \int_{T_O}^{T_{CR}} \left(\frac{10^{-4875/T}}{\phi T^2} \right) dT \quad (21)$$

This gives the final expression for time-to-complete reaction as:

$$t_{CR} = 1.345 \times 10^{-14} T^2 10^{4875/T} \quad (22)$$

The isothermal time to complete reaction (t_{CR}) at a cure temperature of 350°F, by Equation (22), is 3 hr:8 min. A calculation that includes the contribution of the cure cycle steps prior to reaching 350°F, decreases the calculated time needed at 350°F by only a few minutes. Only final cure and postcure temperatures are required.

The mathematical model, equations (7) and (11) predicts the rheology and flow of the resin system under conditions of cure encountered in processing. Equations (19) and (22) constitute a thermokinetic model which uses DSC data to predict conditions of complete cure. Together, these equations are important parts of an overall model which describes the behavior of the resin under conditions of composite processing.

Determine Resin Chemical Properties - The three batches of 3501-6 resin, made from TGMDA base resins with varied viscosities, were tested for chemical properties. The data, shown in Table 9, fall within limits established in earlier work, Reference (1).

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MCDONNELL AIRCRAFT COMPANY**Table 9. Physiochemical Properties**

Batch	Viscosity of TGMDA (CPS) $\times 10^3$	DDS (Total) (%)	Carbonyl Epoxy (Total) (%)	BF ₃ (Total) (%)	DDS (Unreacted) (%)	TGMDA (Unreacted) (%)	Novalac Epoxy (Unreacted) (%)
B-1	11	23.8	8.4	1.1	17.8	53.4	7.3
B-2	14	23.5	8.3	1.3	22.2	53.8	8.9
B-3	18	23.7	8.4	1.3	21.6	50.1	8.5

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The variations in base resin viscosities is due to differences in the type of quantity of oligomers produced in the manufacture of TGMDA. In general, the greater the oligomer content, the higher the viscosity. It was thought that the oligomer content might affect the kinetics of the cure reaction. If this were the case, these three batches, which were all B-staged the same, should have different amounts of unreacted components. However, no significant trends in chemical composition were found.

3.3 PHASE III - DETERMINE RESIN VOLATILES EFFECTS - The objective of this phase was to characterize resin volatiles and their transport and the relationships to voids in the cured system. Exploratory work was conducted relevant to modeling the behavior of volatiles during resin cure.

As a preliminary investigation, samples of as-received 3501-6 neat resin were melted and held at 95°C. At this temperature the resin has an approximate viscosity of 10 poise. Even at this low viscosity no bubbles were formed at ambient pressure. A vacuum of 29" Hg was applied and bubbles quickly formed throughout the resin. The bubbles slowly rose to the surface. After about 45 minutes most of the bubbles had risen to the top one-fourth of the resin. The vacuum was vented and the sample was quickly returned to room temperature. The bubbles in the upper layer of the room-temperature solidified resin were thus "frozen" in place.

The bubble size was measured as a function of resin depth using a Bausch and Lomb Image Analysis System. The bubbles in a given layer were quite uniform in size. The average bubble diameters at nine different depths are given in Table 10. The bubble diameters decrease as the bubbles approach the surface. This would suggest that the bubbles are not coalescing to form larger bubbles as they rise to the surface. The decreasing size of the bubbles as they near the surface is also contrary to what would be expected from hydrostatic pressure effects in a fluid of uniform viscosity.

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MCDONNELL AIRCRAFT COMPANY**Table 10. Variation of Resin Bubble Size with Distance from the Surface**

	Surface Layer					Inner Most Layer				
Distance*	1	2	3	4	5	6	7	8	9	
Bubble Dia (μ)	43	66	77	83	81	98	89	95	95	

*Arbitrary distance with depth of focus

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These preliminary experiments indicated the following:

- o Volatiles present in the as-received 3501-6 resin were capable of producing large quantities of bubbles during resin cure.
- o Of the two suspect volatiles, water and air, absorbed moisture is the most likely candidate, since copious bubble formation resulted only after reducing the pressure on the melted resin to below the vapor pressure of water.

Fabrication of low-void composites thus requires that prepreg production and composite processing conditions be controlled to either remove the resin volatiles or retain them in solid solution.

Direct Observation of Outgassing - A second method used for quantitative assessment of off-gassing characteristics of the resin was a technique reported by Brown and McKaue, Reference (11). This method consists of submerging the specimens in degassed silicone oil and observing the bubble formation during the resin cure cycle. A vacuum oven with a large viewport allowed the use of video equipment to record the out-gassing experiments. The video recording system used provided a continuous readout of time and temperature superimposed above the sample.

Observations and results obtained using this technique included the following:

- o Careful control of the vacuum level above the silicone oil was crucial for reproducibility from run to run. Only prepreg specimens could be compared, since weighted specimens had a tendency to break away from anchors and float to the top of the silicone oil. Making close comparisons required that specimens be observed side by side, during the same run.

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- o As-received AS/3501-6 prepreg was compared with prepreg dried in a vacuum desiccator overnight. The two prepreg specimens were heated at 4-5°F/min to 350°F under vacuum. The as-received material off-gassed vigorously throughout the run, while the dried prepreg showed significantly less off-gassing. Moisture is again indicated as the major volatile. Complete removal of moisture, however, appears difficult and would be a costly step.
- o As-received T300/5208 prepreg was compared with the as-received AS/3501-6 prepreg for conditions of 4-5°F/min heating to hold at 375°F under vacuum. Both specimens bubbled vigorously during most of the run. The 5208 prepreg bubbled more than 3501-6 at 370°F and beyond. This may have been due to the shorter gel time of 3501-6. Otherwise, this technique did not indicate much difference between the two specimens.

Quantitative Introduction of Volatiles - To evaluate volatiles transport mechanisms a method is needed for introducing controlled amounts of the representative volatiles into the matrix resin. Six chemical blowing agents were selected for this purpose and evaluated by DSC. The blowing agents investigated and their exotherm (or endotherm) peak temperatures are given in Table 11.

Table 11. DSC Evaluation of Chemical Blowing Agents, @ 5°C/min

Blowing Agent	Peak Temp., °C
Celogen, TSH (Uniroyal)	168
Celogen, OT (Uniroyal)	166
Kempore (Olin)	209
Opex, 93 (Olin)	203
Nitropore, OBSH (Olin)	155
Expandex (Olin)	(206)

() Endotherm

GP33-9008-27

The maximum rate of gas release should occur at the peak temperatures. On this basis the Nitropore OBSH was selected since it dissociates between the point of minimum viscosity and the on-set of the major reaction exotherm.

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Nitropore OBSH chemically is 4, 4'-oxybis (benzenesulfonhydrazide), which decomposes to give 15% water and 15% nitrogen by weight. This compound was shown to dissolve readily in 3501-6 resin at 90°C and to dissociate at a suitable temperature (155°C) for volatile formation. A known quantity can be introduced of both condensible (H₂O) and noncondensable (N₂) volatiles.

Experimental determinations were made using varied concentrations of Nitropore, i.e., 2, 0.2, and 0.02g Nitropore/100g resin. The mixtures were subjected to cure cycles with and without vacuum. Concentrations in the range of 0.02g Nitropore/100g matrix resin appear to strike a practical balance for future investigations involving volatiles transport mechanisms.

3.4 PHASE IV - RELATE RESIN CHEMORHEOLOGY AND LAMINATE PROPERTIES - The objective of this phase was to determine whether correlation existed between the chemorheology properties determined in the first phases of this program and laminate properties previously reported, Reference (1).

The laminate property data available to this program was limited to the vendor certification and receiving physical and mechanical properties, shown in Tables 12 and 13.

Table 12. Laminate Mechanical Properties

Batch	0° Tensile Properties			Interlaminar Shear		
	Strength (R.T.) (ksi)	Modulus (R.T.) (msi)	Elongation (R.T.) μin./in. × 10 ³	R.T. (ksi)	250°F (ksi)	250°F (ksi) 24 hr Ball
B-1	224, 242, 227 (231)	21.2, 20.0, 19.6 (20.3)	11.0, 12.3, 11.8 (11.7)	21.2, 20.3, 20.8 (20.8)	15.0, 15.0, 15.1 (15.0)	10.4, 10.8, 10.6 (10.6)
B-2	265, 296, 277 (279)	20.1, 21.1, 20.4 (20.5)	13.4, 14.2, 13.8 (13.8)	19.5, 19.6, 19.0 (19.4)	14.6, 13.7, 15.1 (14.5)	11.4, 11.8, 11.5 (11.6)
B-3*	257, 274, 269 (266)	19.4, 20.2, 21.0 (20.0)	13.4, 14.0, 13.3 (13.6)	19.8, 18.5, 18.4 (18.9)	14.6, 14.1, 14.0 (14.2)	12.0, 11.5, 11.4 (11.6)
Minimum Acceptable						
Requirements	200	18.0	10.0	15.0	9.0	7.5

() - Average

*Data from equivalent batch

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MCDONNELL AIRCRAFT COMPANY**Table 13. Laminate Physical Properties**

Batch	Perin Flow (%)	Volatiles (%)	Ply Thickness (in.)	Tac:	% sin Content (%)	Fiber Areal Wt (gm/m ²)
B-1	—	—	0.0051	Conforms	41, 40, 40 (40)	153, 152, 152 (152)
B-2	21.4	0.77	0.0051	Conforms	42, 42, 39 (41)	149, 148, 150 (149)
B-3*	25.9	1.00	0.0050	Conforms	42, 43, 43 (43)	148, 147, 147 (147)
Requirements	10 - 30	1.5 Max	0.0052 + / - 0.0003	Adhere to Itself for 10 min with Less Than 10% Damage	42 ± 3.0	145 - 155

() - Average

*Data from equivalent batch

GP33-0098-25

All batches exceeded the minimum property requirements. No trends were evidenced. Thus, as with the chemorheology, the physical and mechanical tests traditionally used for certification and receiving inspection were insensitive to variations in the viscosity of the TGMDA component within the suppliers specifications.

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4.0 SIGNIFICANT RESULTS

- o A viscokinetic model for the curing behavior of 3501-6 resin was derived from rheometrics and thermal analysis data.
 - The rheological part of the model describes the flow behavior of the resin for any cure cycle using a mathematical expression relating viscosity to the time and temperature of cure.
 - The thermokinetic part of the model describes the conditions required for complete cure using a mathematical expression relating the time for complete cure to the curing temperature.
- o The viscokinetic model, now available, is a pre-requisite for the future development of a composite processing model which includes the effect of the reinforcing fibers.
- o Total resin flow during cure was found to decrease with increased dwell temperature and with increased heating rates.
- o The form of the viscokinetic model for curing behavior of 3501-6 is applicable to other thermosetting resin systems and is proposed as an approach to rapid optimization of curing parameters for future resin systems.
- o The curing behavior was quite similar for three batches of 3501-6 resin in which the base resin (TGMDA) viscosity had been varied across the extreme of currently manufactured MY720 epoxide.
 - A comparison of the rheology of the three batches with their chemical and laminate mechanical properties did not evidence any correlateable inter-relationships.

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5.0 RECOMMENDATIONS

- o Refine the resin rheology model for more exact prediction of experimental viscosity profiles and flow numbers
- o Verify generic applicability of the viscokinetic (rheology and thermokinetic) model to other thermosetting systems.
- o Determine the effects of varied autoclave and vacuum bag pressures on rheology and volatiles transport and off gassing.
- o Determine the effects of the reinforcing fibers on resin rheology and cure.
- o Use a chemical blowing agent for future modeling of the transport properties of condensable and noncondensable volatiles.
- o Volatile matter requires further study because of the deleterious effect in composite properties.

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