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CHEMOVISCOSITY MODELING FOR THERMOSETTING RESINS

By

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T. H. Hou, Co-principal Investigator, and

Surendra N. Tiwari, Principal Investigator

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Final Report
For the period ended August 31, 1985

November 1985

OLD DOMINION UNIVERSITY RESEARCH FOUNDATION

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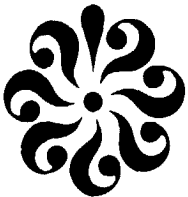
Surendra N. Tiwari, Principal Investigator

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PREFACE

This report covers the work completed on the research project "Chemoviscosity Modeling for Thermosetting Resins" for the period ended August 31, 1985. The work was supported by the NASA Langley Research Center (Polymeric Materials Branch of the Materials Division) under research grant NAG-1-569. The grant was monitored by Mr. Robert M. Baucom of the Polymeric Materials Branch.

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CHEMOVISCOSITY MODELING FOR THERMOSETTING RESINS

By

J. M. Bai[1], T. H. Hou[2] and S. N. Tiwari[3]

SUMMARY

Perkin-Elmer DSC-2 has been upgraded with extra cooling capacity which can support operations down to -40°C. The upgraded equipment has been checked out satisfactorily. Consistent results can be obtained on a routine measurement basis. Data on the degree of cure and the glass transition temperature of Hercules 3501-6 resin system cured under several dynamic heating cure cycles have been measured and documented. These thermal analyses results will be incorporated with the viscoelastic properties of the resin measured by Rheometrics System 4 in the future to establish a model which simulates chemoviscosity rise profiles of reactive resin system under cure.

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I. INTRODUCTION

There are two different basic approaches in chemoviscosity modeling of thermosetting resin. One approach, typically represented by the work of Roller [1], is to empirically formulate a rate equation which relates the change of chemoviscosity with reaction time. For a resin system cured under a dynamic heating cure cycle (as commonly encountered in autoclave processing for composite materials), such an approach usually yields a model which is inadequate in describing accurately the nonlinearity of chemoviscosity as a function of reaction time. As Tajima and Crozier [2] had pointed out that such a modeling approach renders itself to the limitation of batch-specific. The model parameters cannot be readily related to the chemical and rheological properties of the reacting system as well.

The second approach is based upon a modification to the well-established viscosity-temperature relationship existing in polymer rheology for thermoplastic materials. The parameters in such an equation can be expressed in terms of polymerization kinetics, and the chemoviscosity profiles as a function of reaction time can then be modeled for a given thermosetting resin systems.

The applicability of the modified Williams-Landel-Ferry (WLF) theory [3] in chemoviscosity modeling for thermosetting resin has been studied by Tajima and Crozier [2,4], Apicella et al [5], and Hou [6] among others. It has been extensively documented in the literature that temperature-dependent viscosity

of materials, which include low molecular weight (MW) dilute polymer solutions, high MW polymer melts and crosslinked elastomers, can be accurately described by the WLF equations within $100°K$ above its glass transition temperature (T_g). Chemoviscosity profiles are complex due to the fact that they are not only temperature dependent, but also dependent upon reaction kinetics of the particular resin system under study. Consequently the WLF equation has to be modified, before becoming applicable, in such way that the reaction time factor is taken into account.

In an earlier work [6], two assumptions were proposed, namely, that the rate constant of reaction, k_T, at any temperature T, is (i) diffusion controlled and is, therefore, inversely proportional to the viscosity $\eta_T(t)$ of the reactive medium, and (ii) directly proportional to the rate of change of glass transition temperature $T_g(t)$. The modified WLF equation became a first order ordinary nonlinear differential equation. Numerical solutions have also been shown to compare favorably with the experimental results for several thermosetting systems under isothermal and dynamic heating cure conditions. It has been concluded that the flexibility demonstrated by such modified WLF equation can be conveniently exploited to establish an analytical model with high degree of accuracy for the chemoviscosity of any thermosetting resin system under various cure cycles. The physical significances of the material parameters selected for the model were, however, difficult to extract for the particular resin system under investigation.

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The objective of present research is to establish a chemoviscosity model which is capable of not only describing viscosity rise profiles accurately under various cure cycles, but also correlating viscosity data to the changes of physical properties associated with the structural transformations of the thermosetting resin systems during cure.

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II. WORK ACCOMPLISHED

II. Equipments Upgrade

Glass transition temperatures T_g^0 of some unreacted resin systems are possibly below ambient temperature. In order to measure T_g^0 of such system, the current DSC-2 has to be upgraded with additional cooling capacity. An Intercooler II unit has been ordered from Perkin-Elmer for this purpose. The unit could provide supports for DSC-2 operation down to -40°C. In order to prevent moisture condensations on the sample holders while operated in the subambient environment, a package of intermediate range subambient accessory has also been installed. The heating chamber is now enclosed in a dry box, and the sample holders can only be accessed through dry box gloves. A nitrogen purge gas line has been connected as well. Dry box is always purged with nitrogen before measurements started. These devices have been checked out satisfactorily. They are used routinely now for all measurements carried out for this project. More consistent results have been noted since such equipment upgrades were made.

II.2. Measurements of Degree of Cure $\alpha(t)$

The Williams-Landel-Ferry (WLF) equation [3] is given by

$$\log \left(\frac{\eta_T}{\eta_{T_g}}\right) = \frac{-C_1(T-T_g)}{C_2+T-T_g} \qquad (1)$$

for $T_g < T < T_g + 100°K$.

C_1 and C_2 are two material parameters, and η_T represents viscosity at temperature T of the given polymeric material which possesses a glass transition temperature T_g. The normal use of the WLF equation for polymeric materials requires that T_g be constant while the temperature T is varied for the specific polymer under study. However, during cure of thermosetting resins, the monomers are initially polymerized and later crosslinks are formed. This is a system where $T_g(t)$ is changing and the curing temperature T is held constant (in an isothermal cure case, for example). The glass transition temperature T_g rises continuously and may eventually approach the curing temperature. Over the entire curing cycle, the material structure actually undergoes continuous phase transformations from a low molecular weight liquid to a high molecular weight polymeric melt, and eventually transforms to a crosslinked network. It is reasonable to assume that $T_g(t)$ of the material is always lower than the cure temperature T, and

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that $(T-T_g(t))$ is always within 100°K. The WLF equation should then be applicable to all of the different polymeric structure phases during cure.

One method of introducing reaction time factor into Eq. (1) is to express the glass transition temperatures $T_g(t)$ as a function of $\alpha(t)$, the degree of cure. Several different techniques have been used in literature which includes thermal, spectrophotpmetric (FTIR) and chromaographic (HPLC) measurements, to determine the extent of cure. In the present study, we assume that, for the resin system under investigation, $\alpha(t)$ at time t is equal to the fraction of heat released, as measured by DSC, up to time t for the resin system under cure [7,8]. The α's thus determined are function of curing temperature and time.

Several measurements have been made on Hercules 3501-6 resin system under dynamic heating cure conditions with heating rates of 10, 20, 40, 80°K/min, respectively. The total heat of reaction H_T are calculated and tabulated in Table 1. It can be seen that H_T is independent of heating rates. An average value of $H_T = 120 \pm 5.0$ cal/gm was chosen to be used for further analyses.

The degree of cure $\alpha(t)$ have also been calculated and plotted in Figure 1 for resin cured at various heating rates shown. Open and filled symbols represent results from different runs under the same condition. The reproducibilities of the measurements are very satisfactory. Lee et al. [8] had performed DSC thermal analyses on the same resin system studied here. The

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degree of cure α and the rate change of degree of cure $d\alpha/dt$ were examined from the results of the isothermal scanning experiments. Following equations were reported to describe the temperature-dependent data raher accurately:

$$\frac{d\alpha}{dt} = (K_1 + K_2\alpha)(1 - \alpha)(B - \alpha) \qquad \text{for } \alpha \leq 0.3 \qquad (2)$$

$$\frac{d\alpha}{dt} = K_3(1 - \alpha) \qquad \text{for } \alpha > 0.3 \qquad (3)$$

where

$$K_1 = A_1 \exp(-\Delta E_1/RT)$$

$$K_2 = A_2 \exp(-\Delta E_2/RT)$$

$$K_3 = A_3 \exp(-\Delta E_3/RT)$$

and values of constants in Eqs. (2) and (3) are summarized in Table 2.

Eqs. (2) and (3) can be integrated numerically by following cure cycles, respectively, of various heating rates shown in Figure 1. The numerical results are plotted by solid curves in the same figure. Considering the fact that the temperature ranges of 400 to 475°K covered by isothermal experiments, as represented by Eqs. (2) and (3), is narrower than the ranges of 320 to

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600°K covered here by the dynamic heating experiments, the agreements shown in the figure are rather satisfactorily. Figure 1 also implies that information such as chemoviscosity $n(t)$ and degree of cure $\alpha(t)$ under dynamic heating cure conditions can be related within certain accuracy to those obtained under isothermal curing conditions.

II.3. Measurements of Glass Transition Temperatures $T_g(t)$

The technique of measuring $T_g(t)$ of thermosetting resin during cure by DSC can be found in Thermal Analysis Application Study published by Perkin-Elmer [9]. Glass transition temperatures at twelve different states during the advancement of the reactive resin system cured at a constant rate of heating condition of 20°K/min were measured. The measurements were repeated for ten different samples. $T_g(t)$ measured are tabulated in Table 3 together with the degree of cure $\alpha(t)$ measured by the procedures outlined in the last section. Average values of $T_g(t)$ and the standard deviations at different resin states defined by curing time t (or curing temperature T) are included as well. It is noted that standard deviations increase for increasing scanning temperatures. Difficulties in determining T_g accurately come from two sources: (i) the higher the scanning temperatures, the less sharpness for the step change of dH/dt at the glass transition temperature; and (ii) the existence of baseline slope which is usually distorted at higher temperature regimes. Nevertheless, a 90% confidence level can be achieved within ±3% of the experimentally determined values of $T_g(t)$.

Values of $T_g(t)$ are also plotted in Figures 2. It can be noted from the figure that initial increase in $T_g(t)$ is slow. The maximum rate of increase occurs near 525°K, and is in coincidence with the maximum $d\alpha/dt$

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shown in Figure 1. A plot of T_g vs α is shown in Figure 3. A linear relationship is found. The straight line obtained by Least Square fit is

$$T_g(t) = 203.34\ \alpha(t) + 283.5 \tag{4}$$

with a correlation factor $R = 0.9976$.

III.3. CONCLUSIONS

The Perkin-Elmer DSC-2 equipment has been upgraded to provide extra cooling capacity which can support operation down to -40°C. A dry box assembly and nitrogen purge line have also been implemented. The upgrades have been checked out satisfactorily. Routine operations of DSC can yield consistent results.

Experimental measurements have been performed on Hercules 3501-6 resin system under various constant rate of heating cure cycles. Values of degree of cure $\alpha(t)$ obtained from dynamic heating cure experiments are compared favorably with those obtained from numerically integrations of isothermally cured data. It is also demonstrated that chemoviscosity rise profiles for the reactive resin system under dynamic heating cure conditions can be related to those occurred under isothermal cure cycles.

The glass transition temperatures $T_g(t)$ for the resin system cured under constant rate of heating conditions have also been measured. Statistical analysis performed on the results indicated that a 90% confidence level can be achieved with ±3% of the experimentally determined values of $T_g(t)$. A linear relationship between $T_g(t)$ and $\alpha(t)$ has been established. These thermal analyses results will be correlated with chemoviscosity profiles, obtained under same curing conditions, in the future to establish a modified WLF equation for chemoviscosity modeling of thermosetting resins.

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Table 1. Total heat of reaction for Hercules 3501-6 resin system measured at different rate of heating conditions.

No.	Weight mg	Heating Rate °K/min.	Chart. Rec. Speed sec/in.	Range mcal/sec	H_T cal/gm
JMB061085-1	4.6	10	60	0.5	118.702
JMB061185-2	5.5	10	60	0.5	120.129
JMB061185-3	6.4	10	60	0.5	126.472
JMB061085-2	5.2	20	40	0.5	125.311
JMB061185-1	6.7	20	40	0.5	119.474
JMB061185-4	4.3	40	20	1.0	121.55
JMB061185-5	6.7	40	20	1.0	113.14
JMB061385-1	5.7	40	20	1.0	125.37
JMB061185-7	7.6	80	10	2.0	118.34
JMB061385-2	5.3	80	10	2.0	118.32

Heating Rate (°K/min)	Ave. $\overline{H}_T$ (cal/gm)
10	121.77 ± 4.136
20	122.39 ± 4.131
40	120.02 ± 6.26
80	118.3 ± 2.21

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Table 2. Values of constants of Eqs. (2) and (3)
for Hercules 3501-6 Resin System under
isothermal cure conditions

$B = 0.47$

$A_1 = 2.101 \times 10^9 \ min^{-1}$

$A_2 = -2.014 \times 10^9 \ min^{-1}$

$A_3 = 1.960 \times 10^5 \ min^{-1}$

$\Delta E_1 = 8.07 \times 10^4 \ J/mole$

$\Delta E_2 = 7.78 \times 10^4 \ J/mole$

$\Delta E_3 = 5.66 \times 10^4 \ J/mole$

Table 3. Glass transition temperatures measured during reactive advancement of Hercules 3501-6 resin system under 20°K/min rate of heating condition

| Cure Temp T_e(°K) at the end	320	400	425	450	475	500	510	525	535	550	560	575	585
Degree of Cure α	0	0.0001	0.03	0.11	0.23	0.399	0.49	0.645	0.77	0.91	0.96	0.98	
JMB061485-1	284	288		310		356.7		425.3		476.7		486.7	
JMB061785-1	285.3	288		310.6		352		430.7		472		490	
JMB061885-1	283.3	287.3		306.7		364		426		466		490	
JMB061985-1	283.3	286		309.3		353		411.3		468		488	
JMB062085-1	282.6			304.7		348.7		418		463.3		486.7	
JMB061785-2	285.3		294		324		382		434.7		482		
JMB061885-2	284.3		294.7		328		378		444.7		483.3		
JMB061885-3	284.7		298.7		320.7		378		433.3		473.3		
JMB061985-2	283.3		295.3		323.3		371.3		430		474.7		493.3
JMB062085-2	283.3		292		321.3		380.7		437.3		478		
$\overline{T}_g$	283.94	287.33	294.9	308.3	323.47	354.88	378	422.26	436	469.2	478.26	488.28	
$\left[\dfrac{\Sigma(\Delta T_g)^2}{n-1}\right]^{\frac{1}{2}} = \sigma$	0.934	0.943	2.442	2.485	2.882	3.899	4.129	6.318	5.531	5.258	4.38	1.387	

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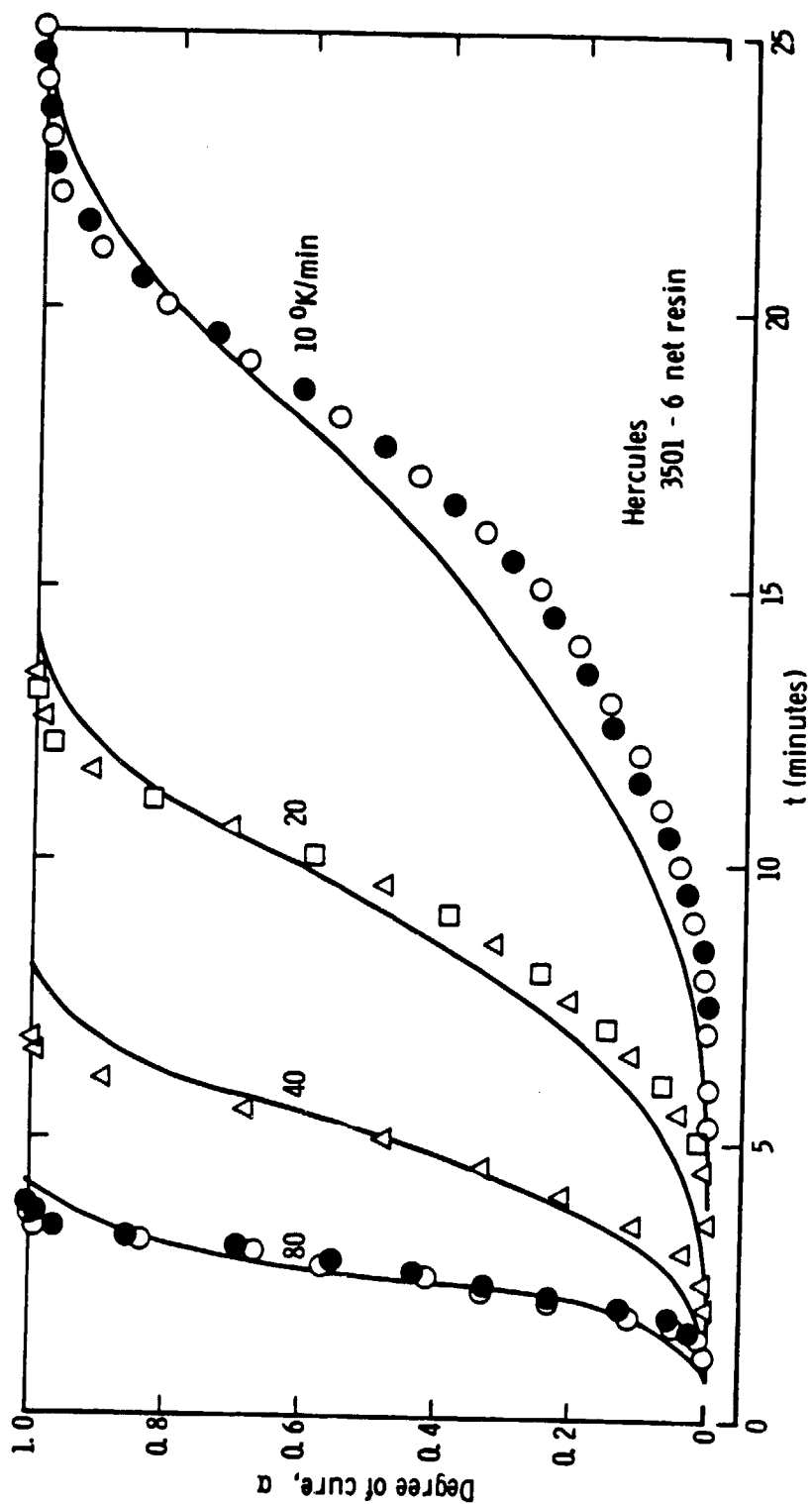
Figure 1. Degree of cure $\alpha(t)$ measured for the Hercules 3501-6 resin system cured under four different rate of heating conditions shown.

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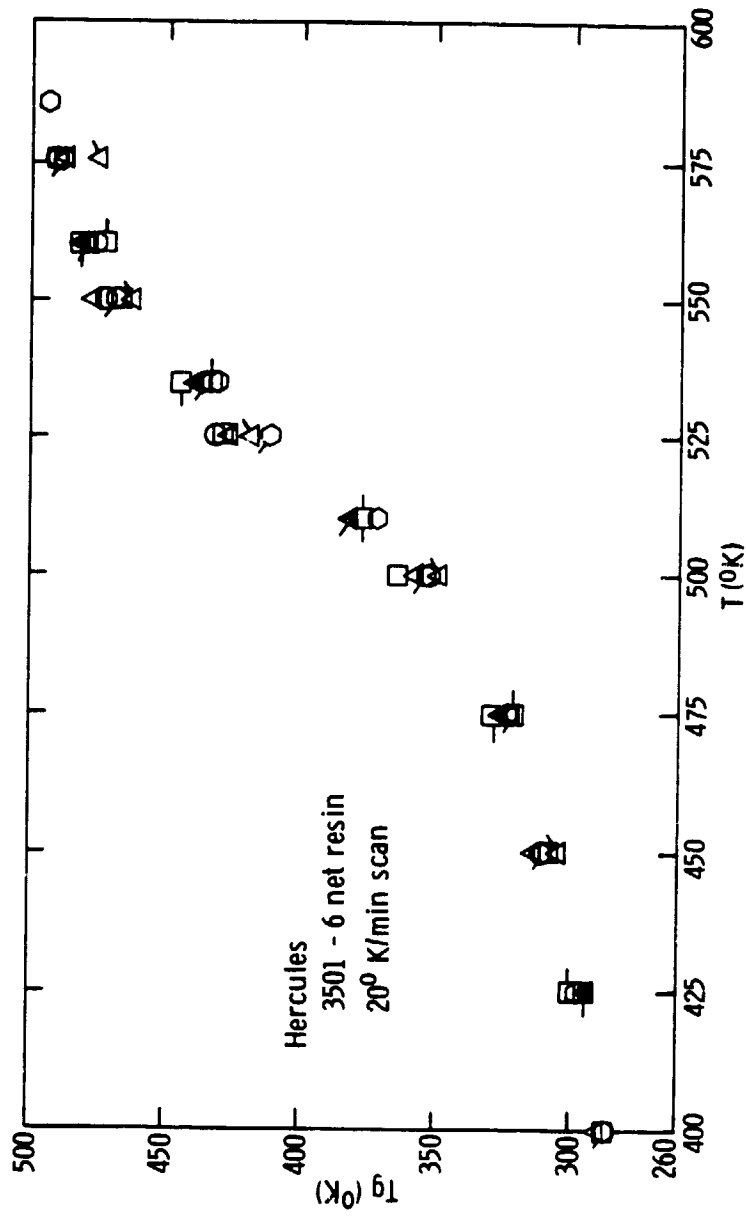
Figure 2. Glass transition temperature $T_g(t)$ measured during reactive advancements of Hercules 3501-6 resin system cured at 20^0 K/min rate of heating condition.
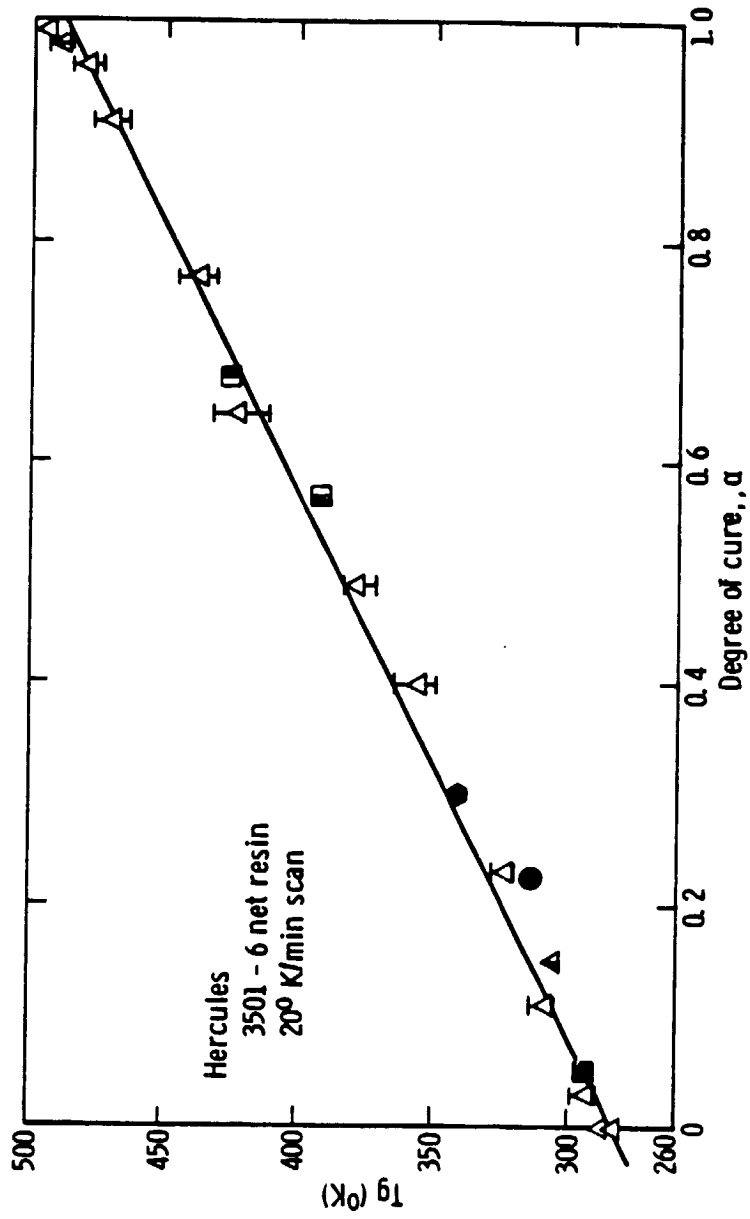
Figure 3. Cross plot of $T_g(g)$ vs. $\alpha(t)$ from Figures 1 and 2.