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# CHEMOVISCOSITY MODELING FOR THERMOSETTING RESINS - I

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          assumptions involved are that the rate of reaction is diffusion controlled
          and is linearly inversely proportional to the viscosity of the medium over
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# CHEMOVISCOSITY MODELING FOR THERMOSETTING RESINS - I

## CONTENTS

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## ABSTRACT

A new analytical model for chemoviscosity variation during cure of thermosetting resins has been developed. This model is derived by modifying the widely used WLF (Williams-Landel-Ferry) Theory in polymer rheology. Major assumptions involved are that the rate of reaction is diffusion controlled and is linearly inversely proportional to the viscosity of the medium over the entire cure cycle. The resultant first order nonlinear differential equation is solved numerically, and the model predictions compare favorably with experimental data of EPON 828/Agent U obtained on a Rheometrics System 4 Rheometer. It has been shown that the model can describe chemoviscosity up to a range of six orders of magnitude under isothermal curing conditions. The extremely non-linear chemoviscosity profile for a dynamic heating cure cycle can be predicted as well. The model is also shown to predict changes of glass transition temperature for the thermosetting resin during cure. The physical significance of this prediction is unclear at the present time, however, and further research is required. From the chemoviscosity simulation point of view, the technique of establishing an analytical model as described here can easily be applied to any thermosetting resin. The model thus obtained can be used in real-time process controls for fabricating composite materials.

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# CHEMOVISCOSITY MODELING FOR THERMOSETTING RESINS - I

## I. INTRODUCTION

Perhaps the single most important property of a polymer with regard to specifying its processing characteristics is its viscosity, which governs the resin flow characteristics. For thermoplastic materials, the viscosity is influenced by local flow geometry and can vary with temperature and shear rate. Viscosity control becomes more critical and difficult in the processing of thermosetting resins, because of the onset of chemical reactions and the generation of heat during curing which causes the viscosity to vary with time. The term chemoviscosity refers to the variation of viscosity due to polymer chemical reaction. The study of chemoviscosity is generally called chemorheology.[1]

In a typical autoclave operation for the fabrication of composite materials,[1] the viscosity-time profile must allow first for the bubbling off of trapped gas, then fiber compaction with resin flow, and, finally, laminate consolidation under applied pressure before the resin has gelled and ceases to flow. At the start of a cure cycle, polymerization begins and the polymer chains lengthen. The increase in viscosity of the resin due to polymerization is, however, largely offset by the increase in temperature which is introduced through the cure cycle and the heat of reaction. Consequently, a drop in resin viscosity of two to three orders of magnitude at the initial stage of cure is not uncommon. As the resin continues to polymerize, crosslinks are formed and the viscosity of the system starts to increase at a faster rate. Finally, the rate of increase of viscosity approaches infinity at gelation. Any chemoviscosity profile is therefore closely related to the reaction kinetics of the resin system and the cure cycle (temperature profile) during processing.

Numerous researchers have devoted considerable efforts to establish an analytical model for the chemoviscosity growth profile of thermosetting resins. The most common approach to this problem has been by empirically specifying the viscosity linearly as an exponential function of reaction time[2-5] or, with the aid of DSC thermal analysis, the degree of cure.[6-7] The uses of such relatively simple models were apparently motivated by the empirically observed nearly linear viscosity growth profiles under isothermal cure conditions. A correlation between such isothermal cure model parameters and the curing temperatures can then be established and used to simulate the chemoviscosity growth in a non-isothermal curing condition such as that encountered inside the autoclave. As expected, the nonlinearity of the viscosity-time profile associated with the advancement of resin cure cannot be accounted for satisfactorily by such models.

The objective of this report is to describe the applicability of the well established Williams-Landel-Ferry (WLF) theory in polymer rheology to the chemoviscosity modeling of thermosetting resins. The viscosity-time profiles under both isothermal and dynamic heating conditions are discussed.

## LIST OF SYMBOLS

| | |
|---|---|
| $c$ | Heating rate (°K/min) |
| $C_1, C_2$ | Constants in WLF Theory, Eq. (1) |
| $C_1^o$ | Initial value of $C_1^i$ selected for the recursion formula Eq. (6a) |
| $k_0, n_0$ | Constants for the parameters in Eq. (6b) |
| $k_{1,2,3,4}$ | Parameters defined in fourth-order Runge-Kutta method |
| $k_T$ | Rate constant of reaction at temperature T |
| $K$ | $\equiv (dT_g/dT)_{T_g}$ |
| $t$ | Time in minutes |
| $t_f$ | Time (min) for complete cure of resin |
| $T$ | Temperature (°K) in cure cycle of thermosetting resins |
| $T_0$ | Starting Temperature (°K) of the cure cycle |
| $T_g(t)$ | Glass transition temperature (°K) of the thermosetting resin during curing |
| $\eta_T(t)$ | Viscosity (poise) growth of the thermosetting resin during the curing temperature T |

## II. THEORY

The Williams-Landel-Ferry (WLF) theory[8] states that for $T_g<T<(T_g + 100°K)$, temperature-dependent viscosity follows the expression:

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

where $C_1$ and $C_2$ are constants. Equation (1) implies that at temperatures above $T_g$ all viscoelastic properties governed by the segmental relaxation rate (e.g., viscous flow, mechanical, and dielectric relaxations, etc.) will vary with temperature in essentially the same way for all polymers. The molecular structure effect on the viscoelastic properties of various polymers will largely disappear when the polymers are compared in corresponding states. The temperature dependency of the viscosity as shown in Equation (1) has been tested and found valid for materials ranging from diluted polymeric systems and thermoplastic melts to rubbers and elastomers.[9] The equation has also been widely used to describe the time-temperature superpositions for the viscoelastic properties of many thermorheologically simple high polymers.[10] Equation (1) can be derived from the semi-empirical Doolittle equation which relates the viscosity to the free volume of the liquid.[11] As the free volume increases, the viscosity rapidly decreases. The two constants $C_1$ and $C_2$ are, therefore, related to the fractional free volume at $T_g$ and the thermal coefficient of expansion of the fractional free volume above $T_g$. $C_1$ and $C_2$ were originally thought to be universal constants with values of 17.44 and 51.6 respectively. It was later found that they are material-related. A tabulation of these material constants for various systems can be found in the literature.[9]

The normal use of the WLF equation for thermoplastic materials requires that the glass transition temperature $T_g$ be constant while the temperature T is varied for the specific polymer under study. Eq. (1) is applicable for a temperature T up to 100°K higher than the $T_g$ of the material. However, during cure of thermosetting resins, the monomers are initially polymerized and crosslinks are formed later. This is a system where $T_g(t)$ is changing and the curing temperature T is held constant, in the isothermal case. 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 the low molecular weight liquid to a high molecular weight polymeric melt, and eventually transforms to form crosslinking networks. If it is assumed that $T_g(t)$ of the material is always lower than the cure temperature T, and that $(T-T_g(t))$ is always within 100°K, then the WLF theory should be applicable to all of the different polymer structure phases during cure. Before Equation (1) can be applied to describe the chemoviscosity of the curing resin, however, modifications have to be made in order to account for the time factor. This can be accomplished by the following rationalizations.

It may be assumed that a segmental relaxation rate governs most rate processes that take place in polymers at temperatures above $T_g$. The rate of reaction is often diffusion controlled, especially in the crosslinking stages. According to the accepted theory of diffusion controlled reactions, the rate constant $k_T$ is generally proportional to the diffusion constant of a reactant, and therefore is inversely proportional to the viscosity of the medium,

$$\frac{\eta_T}{\eta_{T_g}} = \frac{k_{T_g}}{k_T} \qquad (2)$$

It is further assumed that the rate constant of reaction $k_T$ is directly proportional to the rate of change of the glass transition temperature $T_g$,

$$\frac{k_{T_g}}{k_T} = (\frac{dT_g}{dt})_{T_g} / (\frac{dT_g}{dt})_T \qquad (3)$$

Equations (1), (2), and (3) can then be combined to form a first order ordinary nonlinear differential equation:

$$(\frac{dT_g}{dt})_T = K \exp [\frac{C_1(T-T_g)}{C_2+T-T_g}] \qquad (4)$$

where $K = (dT_g/dt)_{T_g}$ is the rate of change of $T_g$ at $T = T_g$, and is taken to be a material constant.

With the boundary condition that as $t \rightarrow t_f$, $T_g \rightarrow T$ where $t_f$ denotes the time for complete cure of the resin and $T$ denotes the cure temperature, Equation (4) can be solved numerically for $T_g$ as a function of curing time, $t$. The chemoviscosity of the curing resin can then be obtained by Equation (1).

In the case of dynamic heating curing conditions, $T$ in Equation (4) can be replaced by $(T_o+ct)$, where $T_o$ is the starting temperature and $c$ is the heating rate in (°C/min). For a given cure cycle (i.e., temperature profile inside the autoclave), two material constants, $\eta_{T_g}$ and $(dT_g/dt)_{T_g}$, and the two WLF constants $C_1$ and $C_2$ need to be specified before Equations (4) and (1) can be solved. Details for solving these equations will be discussed in Section V.

## III. EXPERIMENT DESCRIPTION

A diglycidyl ether of bisphenol A based epoxy resin EPON 828 (Shell) was studied. The hardener selected was a liquid amine EPON Curing Agent U, also from Shell. EPON 828 and Agent U were weighed separately with a microbalance which has a resolution of 0.001 gm. A weight ratio of 100/25 was studied. The two components were hand mixed for 2 minutes before being transferred to a Rheometrics System 4 Rheometer for chemoviscosity measurements.

The sample was confined in the gap between two parallel plates mounted in the Rheometer. The top plate is motor driven about its axis while the bottom plate is mounted on a torque transducer for force measurement. The typical gap between the parallel plates was 1.2 mm. The plates and sample are enclosed in a heat chamber where temperature control is provided. Though the shear field in parallel-plate flow geometry is non-uniform, for the small amplitude displacements used, these effects can be safely neglected. Plate oscillatory motion was set at a frequency of 10 rad/sec, and an amplitude (strain) equivalent of 1 percent of the gap was used for all measurements reported. Selection of the strain value was to assure that the measurements were performed within the material's linear viscoelastic response range.

It is well known that the viscoelastic properties of polymeric materials respond differently to different frequencies, and selection of the frequency value was made to assure that the complex viscosities measured were within the Newtonian region.[12] The cure mode of the Rheometer was used during testing which automatically programs different temperature profiles as the epoxy is cured. Both isothermal and dynamic heating measurements were performed.

## IV. EXPERIMENTAL RESULTS

Chemoviscosity increase profiles for isothermal curing at three different temperatures are shown in Figure 1. The first data point, measured at $t = 0$, corresponds to approximately $5 \pm 0.5$ minutes delay from the beginning of sample mixing in all cases. The initial viscosity is lower when the material is cured at higher temperatures. This is believed to be due to the temperature effect. Figure 1 shows the nonlinearity in the viscosity-time profiles, especially during the initial stages of cure. The profiles become more linear as cure progresses. From the process point of view, the initial stages of cure are far more important because the resin flow is easier to control. A linear chemoviscosity model in this region would certainly be inadequate.

The chemoviscosity profile for a dynamic heating condition is shown in Figure 2. The temperature profile is also included in the figure. The sample is first heated at a rate of 1°C/min from 32°C to 62°C, then the temperature remains constant throughout the cure cycle. The viscosity initially decreases and then increases exponentially. Such viscosity profiles are typical for thermosetting resins under dynamic heating conditions. The decrease in viscosity during the heat up period provides more flexibility in resin flow adjustments for the fabrication of composite materials in an autoclave. Precise chemoviscosity modeling is therefore more important under these conditions.

## V. MODEL PREDICTIONS

### Isothermal case

Using Equation (4), which is rewritten here,

$$\left(\frac{dT_g}{dt}\right)_T = K \exp \left[\frac{C_1(T-T_g)}{C_2+T-T_g}\right] \tag{4}$$

the glass transition temperature $T_g(t)$ can be obtained. The chemoviscosity of the curing resin can then be calculated by

$$\begin{aligned} \eta_T(t) &= \eta_{T_g} \exp \left[\frac{-C_1(T-T_g)}{C_2+T-T_g}\right] \\ &= (\eta_{T_g} \cdot K)/(dT_g/dt) \end{aligned} \tag{5}$$

The two material constants K and $\eta_{T_g}$ have been assigned values of $2 \times 10^{-7}$ °K/min and $1 \times 10^8$ poise, respectively, for all the isothermal model predictions described below. Physically, these two material constants represent the material properties of the resin at the completely cured state.

Constant $C_1$ in the WLF theory is assumed as a function of $T_g$ by the following recursion formula

$$C_1^{i+1} = C_1^{i}(T_g^{i} / T_g^{i+1})^n$$

with (6a)

$$T_g^{i}(t) = T_g(i\Delta t), \; i = 0, 1, 2, \ldots.$$

and

$$n = n_0 e^{k_0 t} \tag{6b}$$

while $C_2$ is assigned the "universal constant" of 51.6°K. The change of $C_1$ as the resin curing progresses (Eq. (6a)) is required by noting that values of $C_1$ vary for different polymeric systems ranging from dilute solutions to cross linked rubbers.[9]

The initial condition, $T_g(0)$ at $t = 0$, is difficult to specify but is required in order to solve the differential Equation (4). Theoretically, $T_g(t_f)$ should be equal to the cure temperature $T$ when the time $t_f$ for the completely cured stage is reached. However, in practice $t_f$ may well approach infinity. In the present study, $T_g(0)$ is arbitrarily chosen, and the simulated results for $T_g(t)$ that were obtained can only describe the relative changes of $T_g$ as a function of time for the resin under study.

The constants used to solve Equations (4), (5), and (6a,b) for the isothermal curing of the EPON 828/Agent U system with weight ratio of 100/25 reported here are summarized in Table 1.

TABLE 1. Constants used in the theory for isothermal case. (EPON 828/Agent U, 100/25 weight ratio)

| Cure Temp. T (°K) | $T_g(0)$ (°K) | K (°c/min) | $\eta_{T_g}$ (poise) | $C_1^0$ | $C_2$ | $n_0$ | $k_0$ |
|---|---|---|---|---|---|---|---|
| 305 | 280 | $2 \cdot 10^{-7}$ | $1 \cdot 10^{8}$ | 41.5 | 51.6 | 1 | 0.165 |
| 310 | 280 | $2 \cdot 10^{-7}$ | $1 \cdot 10^{8}$ | 38 | 51.6 | 1 | 0.245 |
| 317 | 280 | $2 \cdot 10^{-\Lambda}$ | $1 \cdot 10^{8}$ | 37 | 51.6 | 1 | 0.385 |

Equation (4) is solved numerically by a fourth-order Runge-Kutta method[13] as modified by Gill:

$$
\begin{aligned}
T_g^{i+1} &= T_g^{i} + \frac{h}{6}\left[k_1 + 2\left(1 - \frac{1}{\sqrt{2}}\right) k_2 + 2\left(1 + \frac{1}{\sqrt{2}}\right) k_3 + k_4\right] \\
k_1 &= f(t^i, T_g^i) \\
k_2 &= f\left(t^i + \frac{h}{2}, T_g^i + \frac{h}{2} k_1\right) \\
k_3 &= f\left(t^i + \frac{h}{2}, T_g^i + \left(-\frac{1}{2} + \frac{1}{\sqrt{2}}\right)hk_1 + \left(1 - \frac{1}{\sqrt{2}}\right)hk_2\right) \\
k_4 &= f\left(t^i + h, T_g^i - \frac{1}{\sqrt{2}} hk_2 + \left(1 + \frac{1}{\sqrt{2}}\right)hk_3\right)
\end{aligned}
\qquad (7)
$$

where h is the time increment and

$$f(t, T_g) = K \exp\left[\frac{C_1(T-T_g)}{C_2+T-T_g}\right] \qquad (8)$$

This algorithm was programmed in Basic and solved on a Hewlett-Packard HP-9836 computer. The program listing is included in the Appendix for reference.

Numerical solutions are plotted in Figure 1 with the experimental data for isothermal curing at three temperatures. Good agreement between the data and theory for all three cases are noted. The capability of the model to describe up to six orders of magnitude in chemoviscosity range is significant. Numerical computations were performed for different time increment ($\Delta t$ and $h$ in Eq. (6a) and (7), respectively). It was found that the simulated chemoviscosities based on $\Delta t = 0.5$ and 0.25 minutes, respectively, differ by less than 1% for all three temperatures. The simulated initial viscosities for various temperatures are the result of different assigned values of $C_1^0$ and $n_0$, while the simulated viscosity increase rates are dictated by the assigned $k_0$. Variations of the computed $C_1$ are plotted in Figure 3. It is noted in the literature[9] that $C_1$ varies from 11.2 for polybutadiene rubber to 34.0 for Methyl (atactic) polymer. The variations of $C_1$ shown dictate structure changes of the material under investigation, and are approximately equivalent to a variation from 0.011 to 0.087 for $f_g$, the fractional free volume at $T_g$, of the curing resin.

Calculated values for $T_g(t)$ for the curing resin are also shown in Figure 3. It can be noted that changes of $T_g$ are faster for higher cure temperatures during early curing stages. Higher cure temperatures yield higher $T_g$. After the initial curing period of approximately 20 minutes, values of $T_g$ quickly level off; the chemoviscosities $\eta(t)$, however, keep increasing as can be seen from Figure 1. Similar situations exist in the relationship between $\eta(t)$ and $\alpha(t)$, the degree of cure determined by DSC thermal analysis, as reported experimentally by Lee et al.[7] These observations imply that determinations of gelation points of the thermosetting resins by viscosity data alone are questionable. Further research in this area is planned. $T_g(t)$ in Figure 3 increases very slowly after the initial 20 minutes, and may take a very long time to reach cure temperatures of 305, 310, and 317°K, respectively. This is in agreement with the fact that low curing temperatures are employed.

The analytical model developed here (i.e., Eqs. (4), (5), and (6a,b)) possesses three material constants and four adjustable parameters. In describing the chemoviscosity under isothermal curing, however, only two parameters ($C_1^0$ and $k_0$ in Table 1) need to be adjusted in order to account for the differences in cure temperatures. It can be noted from Figure 1 that the model predictions are in better agreement with the experimental data than the empirical 4-parameter model used in the literature[3]. The values of $C_1^0$ and $k_0$ used follow the Arrhenius relationship shown in Figure 4. The Arrhenius correlation makes chemoviscosity predictions possible for this material at temperatures outside the range studied here.

## Dynamic Heating Case

In this case cure temperature changes with time. The value of T in Equations (4) and (5) is replaced by ($T_0$ + ct), where $T_0$ is the start temperature and c is the rate of increase of the temperature. Equation (4) becomes

$$\frac{dT_g}{dt} = K \exp \left[\frac{C_1(T_0+ct-T_g)}{C_2+T_0+ct-T_g}\right] \tag{9}$$

When Equation (9) is directly applied to the cure cycle shown in Figure 2 using the material constants listed in Table 1, the predictions as plotted by the dashed line are relatively poor. The drop in viscosity in the initial cure portion is overestimated, and the rate of viscosity increase as the cure progresses is not as high as those experimentally measured. By selecting the following new set of constants: $K = 9.2 \times 10^{-7}$, $C_1^0 = 41.0$ and

$$\begin{array}{llll} n_o = 1, & k_o = 0, & \text{for} & 0 < t < 15 \text{ mins} \\ \quad = 0.00012, & \quad = 0.62, & & 15 < t < 21 \\ \quad = 0.00012, & \quad = 0.59, & & 21 < t \end{array}$$

the simulated results shown by solid line in Figure 2 are in very close agreement with the experimental data.

When numerical computations were performed for two different time increments ($\Delta t = 0.5$ and $0.25$), the values of calculated chemoviscosity differed by less than 1%. The variations of $T_g(t)$ and $C_1(t)$ during cure are shown in Figure 5. The behaviors of $T_g$ and $C_1$ are very similar to those discussed before under isothermal cure cases.

The theory was also compared with dynamic heating cure data reported by Tajima and Crozier.[1] The material used was composed of two epoxy resins, TGMDA-MY720 of 69 wt. percent and SU-8 of 9 wt. percent, and an amine hardener DDS of 22 wt. percent. The cure cycle for this resin together with the chemoviscosity data are reproduced in Figure 6. Material constants selected for the model are as follows:

$$T_g(0) = 284°K, \; K = 2 \cdot 10^{-10} \text{ °k/min}$$

$$\eta_{T_g} = 1 \times 10^{10} \text{ poises}, \; C_1^0 = 31.6, \; C_2 = 51.6°K$$

$$\begin{array}{llll} \eta_o = 0.1, & k_o = .001, & \text{for} & 0 < t < 71 \text{ min} \\ \quad = 0.0002, & \quad = 0.1, & & 71 < t < 111 \\ \quad = 4 \times 10^{-5}, & \quad = 0.1, & & 111 < t < 121 \\ \quad = 1 \times 10^{-5}, & \quad = 0.115, & & t > 121 \end{array}$$

Excellent agreement was demonstrated between the model predictions and experimental data. Variations of $T_g(t)$ and $C_1(t)$ during cure are also plotted in Figure 7. The behaviors of these quantities are similar to those discussed before for the Epon 828/Agent U system.

Equations (6a) and (6b) have been incorporated in Equation (4) or (9) to simulate the chemoviscosity of thermosetting resins under various cure cycles discussed so far. Equations (6a) and (6b) are, however, purely empirical. Other forms can also be successfully used. For example, consider the following new equation:

$$C_1 = C_1^0 \; [1 + \log(\frac{T_g}{T})^{k_o}] \tag{10a}$$

and the recursion formula for $k_o$ as

$$k_o^{i+1} = k_o^{i} \times (T_g^{i+1}/T_g^{i}) \times \eta_o \tag{10b}$$

Material constants selected for this model are as follows:

$$T_g(o) = 46°K, \quad K = 5 \times 10^{-14} \; °K/min$$

$$\eta_{T_g} = 1 \cdot 10^{13} \text{ poises}, \quad C_1^0 = 32.44, \quad C_2 = 51.6°K$$

while

$$\begin{array}{llll} n_o = 0.98, & k_o^0 = 0.19, & \text{for} & 0 < t < 75 \text{ min} \\ \phantom{n_o} = 1.025, & \phantom{k_o^0} = 0.19, & & 75 < t < 111 \\ \phantom{n_o} = 1.008, & \phantom{k_o^0} = 0.19, & & t > 111 \end{array}$$

When the temperature profile in Figure 8 is followed, Equations (9), (10a), and (10b) give solutions plotted as the solid curve in Figure 8. The model predictions again agree well with the experimental data over the entire cure cycle.

Tajima and Crozier[1] used the same WLF Theory to explain their experimental data. However, the treatments are quite different from those described in this paper. They choose reference temperatures $T_s(t)$ to replace $T_g(t)$ in Eq. (1). While both $\eta_{T_s}(t)$ and $T_s(t)$ are varied, the constants $C_1$ and $C_2$ are kept constant during the entire cure cycle. The values of $\eta_{T_s}(t)$ and $T_s(t)$ are related to the content of unreacted curing agent (DDS) where the time factor is introduced. Physically, continuous changes of reference viscosity and temperature in the WLF theory imply continuous changes in molecular structures of the material. This accounts for the good agreement between their model and the experimental data. The approach reported in this paper involves only one experiment (i.e. Rheometry) and the model is much easier to establish.

Mussatti and Macosko[14] reported steady shear viscosity data on EPON 828 catalyzed by 1% by weight of triethanolamine (TEA) under isothermal curing at 100°C. Viscosity measurements were made with cone and plate flow geometry of a Rheometrics Mechanical Spectrometer. Rotation was started and stopped periodically as the reaction proceeded, and the resulting torque was recorded until the sample broke up. The viscosity data obtained in this experiment are reproduced in Figure 9. Attempts have also been made to fit the data with the model, i.e., Eqs. (10a,b) for the parameters $C_1$ and $k_0$ have been used together with the model Eq. (4). Material constants and parameters selected for the model are as follows:

$T_g(0) = 150°K$, $K = 5.0 \times 10^{-14}$ °K/min

$\eta_{Tg} = 1 \times 10^{13}$ poises, $\overset{\circ}{C_1} = 38.44$, $C_2 = 51.6°K$

and

$\eta_0 = 1.01$ , $k_0 = 0.1$, for $0 < t < 50$ mins

$= 1.045$, $= 0.1$ $50 < t < 60$

$= 1.022$, $= 0.1$ $t > 60$

It can be seen in Figure 9 that the theory can also describe the steady shear viscosity data very well. Variations of $T_g(t)$ and $C_1(t)$ during cure are plotted in Figure 10 for reference. The behaviors of these quantities are again similar to those discussed before for other resin systems.

## VI. CONCLUSIONS

It has been shown that the WLF theory, Equations (4) and (9), with the appropriately selected material constants can accurately predict the chemoviscosity of thermosetting resins. The success in applying the theory to an entire cure cycle for both isothermal and dynamic heating conditions indicate valid assumptions for chemoviscosity model development. It is surprising to note that the simple assumption of Eq. (2) (where viscosity is assumed to be linearly inversely proportional to the rate constant of reaction) incorporated with WLF theory can account for the chemoviscosity increase over an entire cure cycle. The demonstrated capability to describe up to six orders of magnitude of change in the chemoviscosity range with the model is significant. The model can also predict the change of glass transition temperature $T_g(t)$ during cure. The physical significance of the predicted $T_g(t)$ which results from the assumption of Eq. (3) in the theory is unclear at the present time. A thorough understanding of the kinetics of chemoviscosity, the degree of cure, the stoichiometry and mechanism of polymerization can only be achieved by a combined use of several analytical methods, such as Rheometry, DSC, TBA, and spectroscopy. Such tasks remain to be resolved in the future.

The model as described has considerable value in autoclave process monitoring applications. An analytical model with the appropriate parameters determined from a single set of experimental data (e.g., via Rheometry) can easily be established for any thermosetting resin. The established model, which has the capability of describing the chemoviscosity accurately, can be used in real-time control of automatic composite processing equipment when an appropriate sensing device can be identified.

## REFERENCES

1. Tajima, Y. A.; and Crozier, D.: "Thermokinetic Modeling of an Epoxy Resin I. Chemoviscosity," Polym. Engr. Sci., 23, 186, 1983.
2. Roller, M. B.: "Characterization of the Time-Temperature-Viscosity Behavior of Curing B-Staged Epoxy Resin," Poly. Engr. Sci., 15, 406, 1975.
3. Carpenter, J. F.: "Processing Science for AS/3501-6 Carbon/Epoxy Composites," Technical Report N00019-81-C-0184, McDonnell Aircraft Co., 1983.
4. Kamal, M. R.; Sourour, S.; and Ryan, M.: "Integrated Thermo-Rheological Analysis of the Cure of Thermosets," Technical Papers, 31st Annual Technical Conference, SPE, 187, 1973.
5. Kamal, M. R.: "Thermoset Characterization for Moldability Analysis," Polym. Engr. Sci., 14, 231, 1974.
6. Stolin, A. M.; Merzhanov, A. G.; and Malkin, A. Y.: "Non-Isothermal Phenomena in Polymer Engineering and Science: A Review. Part II: Non-Isothermal Phenomena in Polymer Deformation," Polym. Engr. Sci., 19, 1065, 1979.
7. Lee, W. I.; Loos, A. C.; and Springer, G. S.: "Heat of Reaction, Degree of Cure, and Viscosity of Hercules 3501-6 Resin," J. Compo. Matl., 16, 510, 1982.
8. Williams, M. L.; Landel, R. F.; and Ferry, J. D.: "The Temperature Dependence of Relaxation Mechanisms in Amorphous Polymers and Other Glass-forming Liquids," J. Amer. Chem. Soc., 77, 3701, 1955.
9. Ferry, J. D.: "Viscoelastic Properties of Polymers," 2nd ed., pp. 316, John Wiley & Sons, Inc., 1970.
10. Kaniskin, V. A.; Kaya, A.; Ling, A.; and Shen, M.: "Mechanical and Dielectric Relaxations in Alternating Block Copolymers of Dimethylsiloxane and Bisphenol A Carbonate," J. Appl. Polym. Sci., 17, 2695, 1973.

11. Aklonis, J. J.; MacKnight, W. J.; and Shen, M.: "Introduction to Polymer Viscoelasticity," pp. 53, John Wiley & Sons, Inc., 1972.

12. Bird, R. B.; Armstrong, R. C.; and Hassager, O.: "Dynamics of Polymeric Liquids, Vol. 1," pp. 194, 1977.

13. Carnahan, B.; Luther, K. A; and Wilkes, O. J.: "Applied Numerical Methods," pp. 363, John Wiley & Sons, Inc., 1969.

14. Mussatti, F. G.; and Macosko, C. W.: "Rheology of Network Forming Systems," Polym. Engr. Sci. 13, 236, 1973.

## APPENDIX

Shown herein is a listing for solving Eqs. (4), (5), (6a,b) by means of a Runge-Kutta algorithm. Hewlett-Packard Basic Extension 2.0 language is used. The program is run on a HP-9836 computer.

```
10     ! 2/8/84. "DIFFER3_A0"
20     ! 2/15/84. REVISED ! TO ACCOMMODATE BOTH CONST AND NONISO-THERMAL CASES
30     !
40     ! THIS PROGRAM FIXES FINAL CURING TEMP = T AT TIME=TFINAL
50     ! ADJUSTABLE VARIABLES ARE K,A.B FOR THE NON-ISOTHERMAL CASE
60     ! NUMERICAL SOLUTIONS ARE PROVIDED BY SHOOTING METHOD IN-
70     ! CORPORATED WITH THE RUNGE-KUTTA 4TH ORDER SCHEME TO SOLVE
80     ! THE DIFFERENTIAL EQUATION
90     !     IT HAS BEEN ASSUMED THAT K=(DTG/DT) AT TG IS A CONSTANT;
100    !     THAT A(I)=A0(I)*(TG(I)/TG(I+1))^N,  A(I)=C1
110    !          B=51.6. B=C2 IN WLF THEORY
120    ! ......CONST AND  NON-ISOTHERMAL CASE ........
130    !
140    COM Timechg0.Timechg1.Timechg2.Timechg3.Cc.A0
150    COM Tg0temp.Tg0last,Tg0now.Alast.Anow
160    COM Nn.N0,N1.N2.N3,Kn1.Kn2.Kn3.Kn4,Kn5.Kn6.Kn7.Kn8
170   !
180     Tg0=284
190     K=2.0E-10
200        A0=31.6
210        N0=.1
220        Kn2=.001
230        Timechg0=71
240   !
250        N1=.0002
260        Kn4=.1
270        Timechg1=111
280   !
290        N2=.00004
300        Kn6=.1
310        Timechg2=121
320   !
330        N3=.00001
340        Kn8=.115
350        Timechg3=2000
360   !
370    LET A=A0
380    LET B=51.6
390        C1st=1.
400        C2nd=.8
410        Time1=70
420        Time2=115
430        Tstart=338
440        Temp=Tstart
450        Tfinal=1000
460        Xxtg=1.E+10
470   !
480        H=.5
490   !
500    PRINT "DIFFER3_A0_CROZIER2"
510    PRINT
520    PRINT "SOLUTIONS FOR TSTART(K)=";Tstart;"      TFINAL(MIN)=";Tfinal
530    PRINT "A0=";A0;"B=";B;"K=";K;"H=";H
540    PRINT "TEMP PROFILE IS C1ST=";C1st;" AT TIME1=";Time1
550    PRINT "                AND C2ND=";C2nd;" AT TIME2=";Time2
560    PRINT "TIMECHG0=";Timechg0;"N0=";N0;"KN1=";Kn1;"KN2=";Kn2
570    PRINT "TIMECHG1=";Timechg1;"N1=";N1;"KN3=";Kn3;"KN4=";Kn4
580    PRINT "TIMECHG2=";Timechg2;"N2=";N2;"KN5=";Kn5;"KN6=";Kn6
590    PRINT "TIMECHG3=";Timechg3;"N3=";N3;"KN7=";Kn7;"KN8=";Kn8
600    PRINT "XXTG=",Xxtg
610    PRINT
```

```
620   ! ------------------------------------------------------------------
630    Time0=0.
640    Clock=1
650    Dtgdt=FNValue(Time0.Tg0.A.B.Time0,K.Tstart.Tstart)
660    Xx=Xxtg*K/Dtgdt
670       PRINT Time0.Tg0,"          ".Dtgdt."XX=".Xx
680       PRINT
690   !  TEMPERATURE PROFILE IS DEFINED AS FOLLOWS:
700                IF Time0<Time1 THEN
710                Cc=C1st
720                Temp=Tstart+Cc*Time0
730                Tempnow=Tstart+Cc*(Time0+H)
740                GOTO 880
750                ELSE
760                GOTO 770
770                END IF
780                IF Time0<Time2 THEN
790                Cc=0
800                Temp=Tempnow
810                Tempnow1=Temp
820                GOTO 880
830                ELSE
840                Cc=C2nd
850                Temp=Tempnow1+C2nd*(Time0-Time2)
860                Tempnow=Tempnow1+Cc*(Time0+H-Time2)
870                END IF
880       CALL Runge_kutta(Time0.Tg0.H,Tgnew,A.B.Time0.K,Tstart,Temp)
890       Tg0=Tgnew
900       Tg0last=Tg0temp
910       Tg0now=Tg0
920       Alast=Anow
930       Timenow=Time0+H
940       Dtgdt=FNVal0(Anow,B.Timenow,Tg0.K,Tempnow)
950       Xx=Xxtg*K/Dtgdt
960         IF Timenow>Tfinal THEN
970         GOTO 1100
980         ELSE
990         GOTO 1010
1000        END IF
1010            IF Timenow=Clock THEN
1020            Clock=Clock+5
1030            PRINT Timenow;Tempnow:Tg0:Dtgdt:"XX=":Xx:Anow
1040            Time0=Time0+H
1050            GOTO 700
1060            ELSE
1070            Time0=Time0+H
1080            GOTO 700
1090            END IF
1100    END
1110 !  ---------------------------------------------------------------
1120 !
1130    SUB Runge_kutta(Xi.Yi.H.Yi1.A.B.Time.K.Tstart.Temp)
1140       COM Timechg0,Timechg1,Timechg2.Timechg3.Cc.A0
1150       COM Tg0temp.Tg0last.Tg0now.Alast.Anow
1160       COM Nn,N0,N1,N2,N3,Kn1,Kn2.Kn3,Kn4,Kn5.Kn6.Kn7,Kn8
1170       Tg0temp=Yi
1180       K1=FNValue(Xi.Yi.A.B.Time.K.Tstart.Temp)
1190          Xt=Xi+H/2.
1200          Yt=Yi+H/2.*K1
1210          Tempp=Temp+Cc*H/2.
1220       K2=FNValue(Xt.Yt.A.B.Time.K.Tstart.Tempp)
```

```
1230          Xt=Xi+H/2.
1240          Yt=Yi+(-.5+1./SQR(2.))*H*K1+(1.-1./SQR(2.))*H*K2
1250       K3=FNValue(Xt,Yt,A,B,Time,K,Tstart,Tempp)
1260          Xt=Xi+H
1270          Yt=Yi-(1./SQR(2.))*H*K2+(1.+1./SQR(2.))*H*K3
1280          Tempp=Temp+Cc*H
1290       K4=FNValue(Xt,Yt,A,B,Time,K,Tstart,Tempp)
1300       V1=2.*(1.-1./SQR(2.))
1310       V2=2.*(1.+1./SQR(2.))
1320       Yi1=Yi+H/6.*(K1+V1*K2+V2*K3+K4)
1330       SUBEND
1340    ! ------------------------------------------------------------
1350    !
1360    DEF FNValue(X,Y,A,B,Time,K,Tstart,Temp)
1370     COM Timechg0,Timechg1,Timechg2,Timechg3,Cc,A0
1380     COM Tg0temp,Tg0last,Tg0now,Alast,Anow
1390     COM Nn,N0,N1,N2,N3,Kn1,Kn2,Kn3,Kn4,Kn5,Kn6,Kn7,Kn8
1400       T0=Temp
1410             IF Time=0 THEN
1420             Nn=N0
1430             Tg0now=Y
1440             Tg0last=Y
1450             Alast=A0
1460             GOTO 1740
1470             ELSE
1480             GOTO 1490
1490             END IF
1500       IF Time<Timechg0 THEN
1510       Nn=N0*EXP((Time)*Kn2)
1520       GOTO 1740
1530       ELSE
1540       GOTO 1550
1550       END IF
1560              IF Time<Timechg1 THEN
1570              Nn=N1*EXP(Time*Kn4)
1580              GOTO 1740
1590              ELSE
1600              GOTO 1610
1610              END IF
1620          IF Time<Timechg2 THEN
1630          Nn=N2*EXP(Time*Kn6)
1640          GOTO 1740
1650          ELSE
1660          GOTO 1670
1670          END IF
1680               IF Time<Timechg3 THEN
1690               Nn=N3*EXP(Time*Kn8)
1700               GOTO 1740
1710               ELSE
1720               GOTO 1730
1730               END IF
1740     !
1750        Anow=Alast*(Tg0last/Tg0now)^Nn
1760        A=Anow
1770        B=B
1780        T1=A*(T0-Y)
1790        T2=B+T0-Y
1800        T3=T1/T2
1810        Value=K*EXP(T3)
1820        RETURN Value
1830        FNEND
```

```
1840      !
1850      !
1860   DEF FNVal0(A0,B0,Time0,Tg0,K,Temp1)
1870        A=A0
1880        B=B0
1890        T1=A*(Temp1-Tg0)
1900        T2=B+Temp1-Tg0
1910        T3=T1/T2
1920        Value1=K*EXP(T3)
1930        RETURN Value1
1940        FNEND
1950        !
1960        !
```

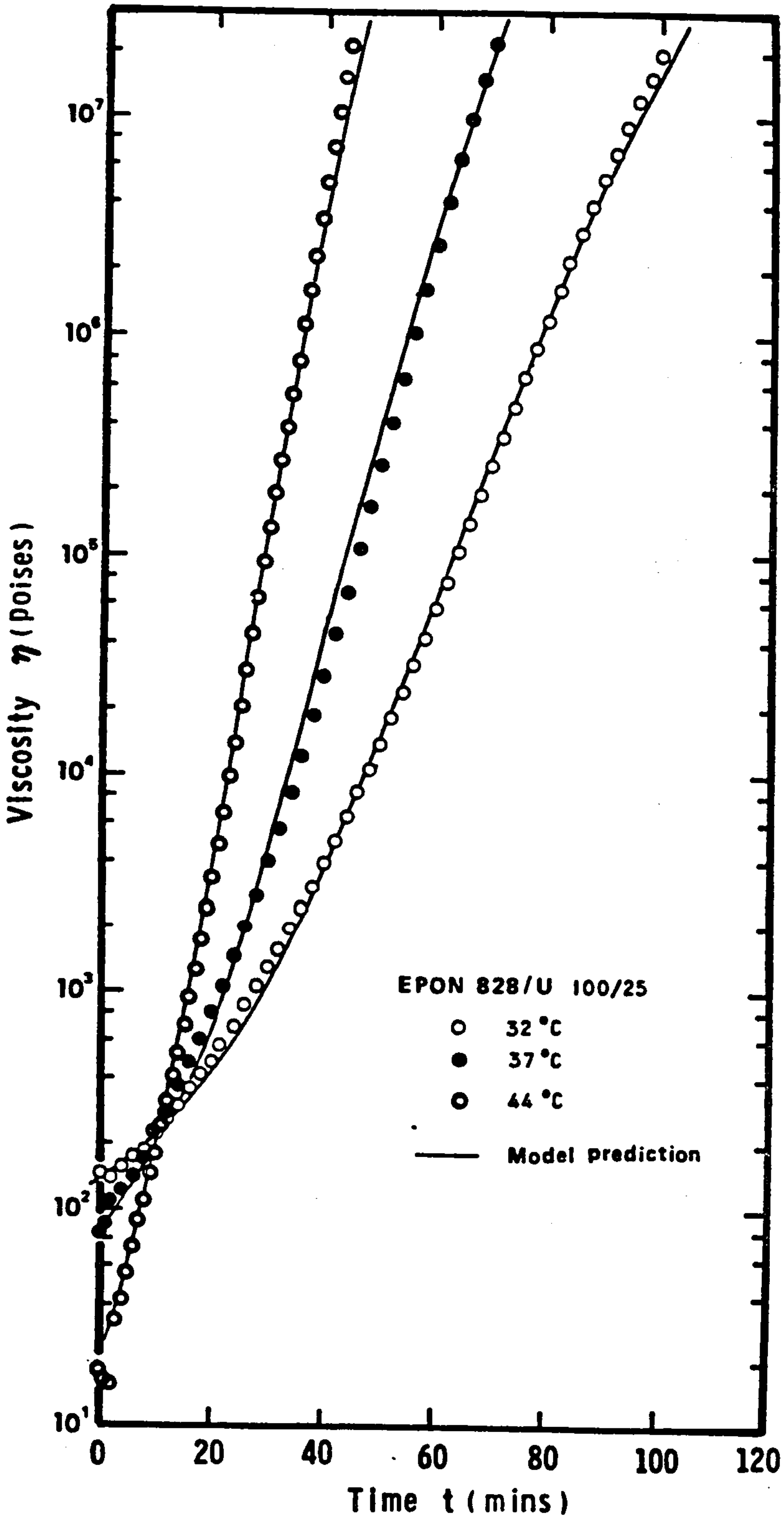

Figure 1. Comparisons between experimental chemoviscosity data and the model predictions for EPON 828 with Agent U. Chemoviscosity of the resin is measured by Rheometrics System 4 Rheometer under three isothermal curing conditions.

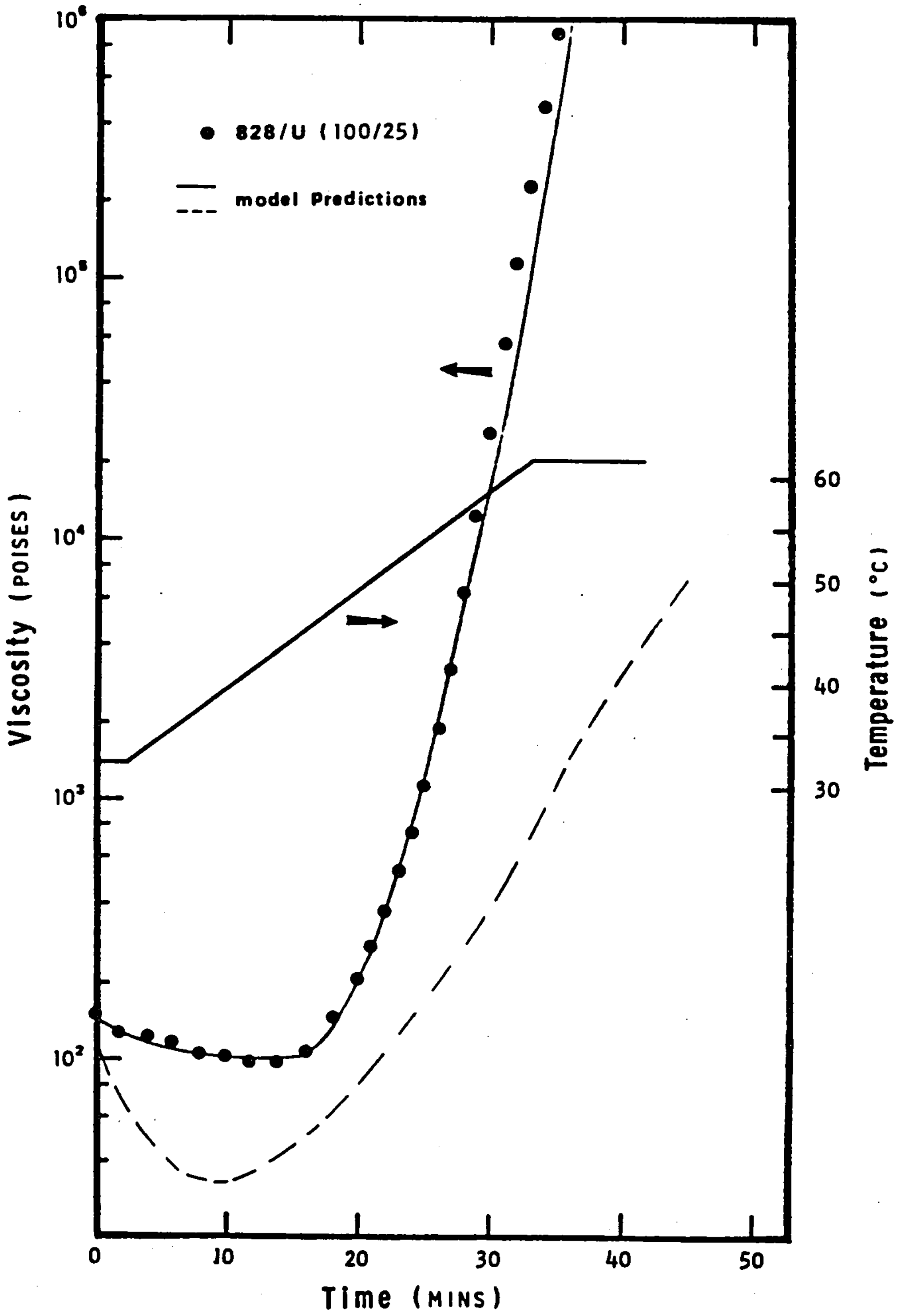

Figure 2. Comparisons between experimental non-isothermal chemoviscosity and the model predictions for EPON 828 with Agent U. Chemoviscosity of the resin is measured by Rheometrics System 4 Rheometer. The cure cycle (temperature profile) is also shown.

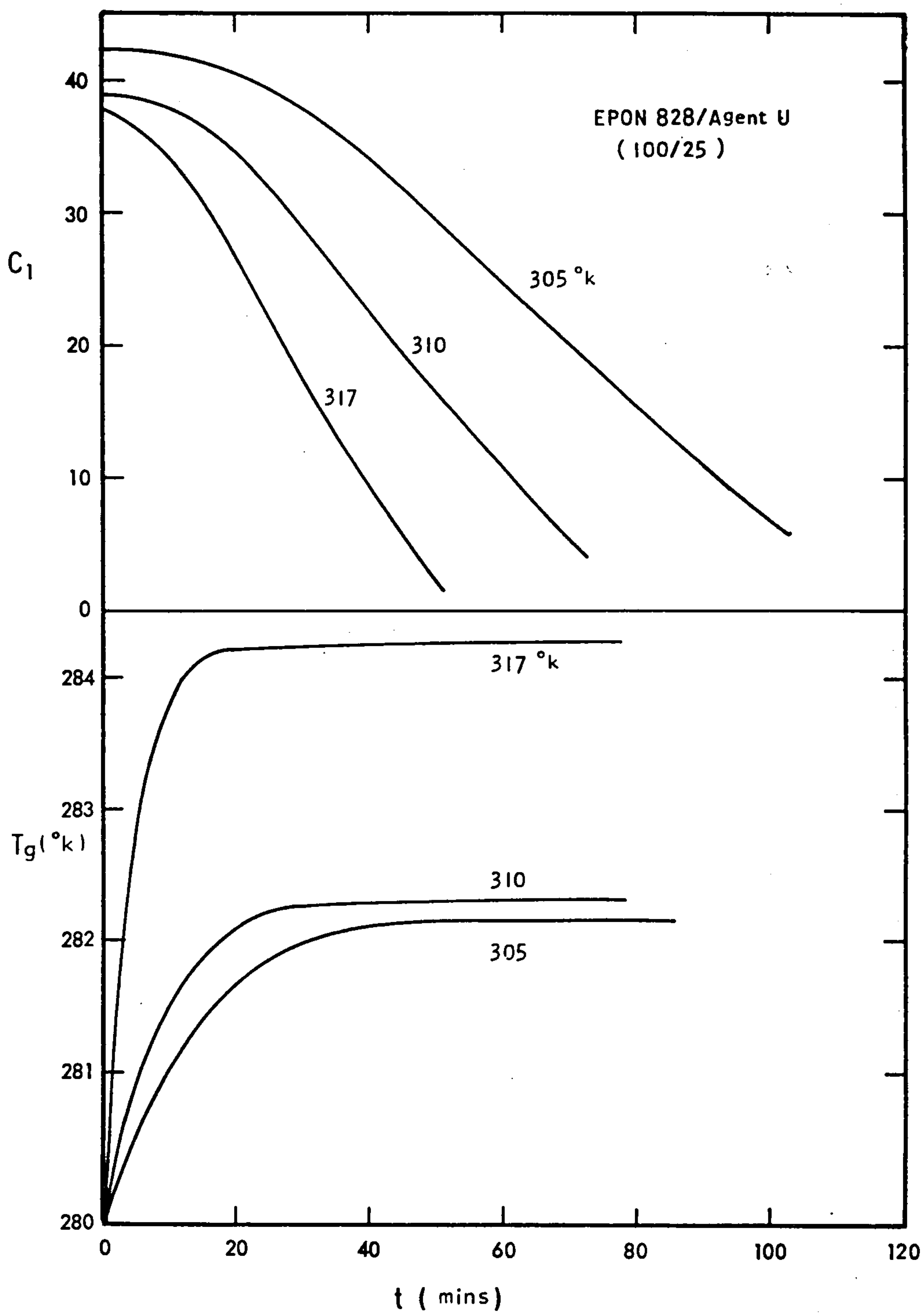

Figure 3. Variations of $T_g(t)$ and $C_1$ during cure obtained from the simulation models in Figure 1 for EPON 828/U resin system under isothermal curing conditions.

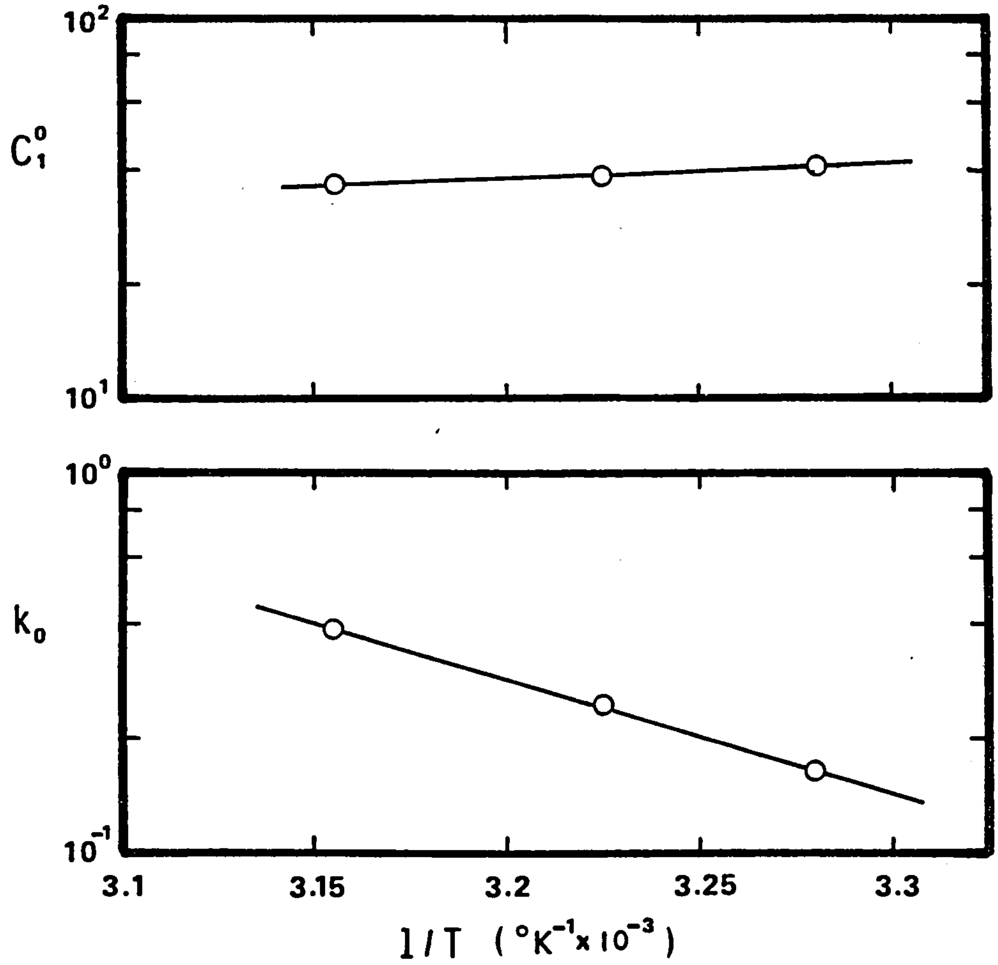

Figure 4. Arrhemius relationship for the model parameters.

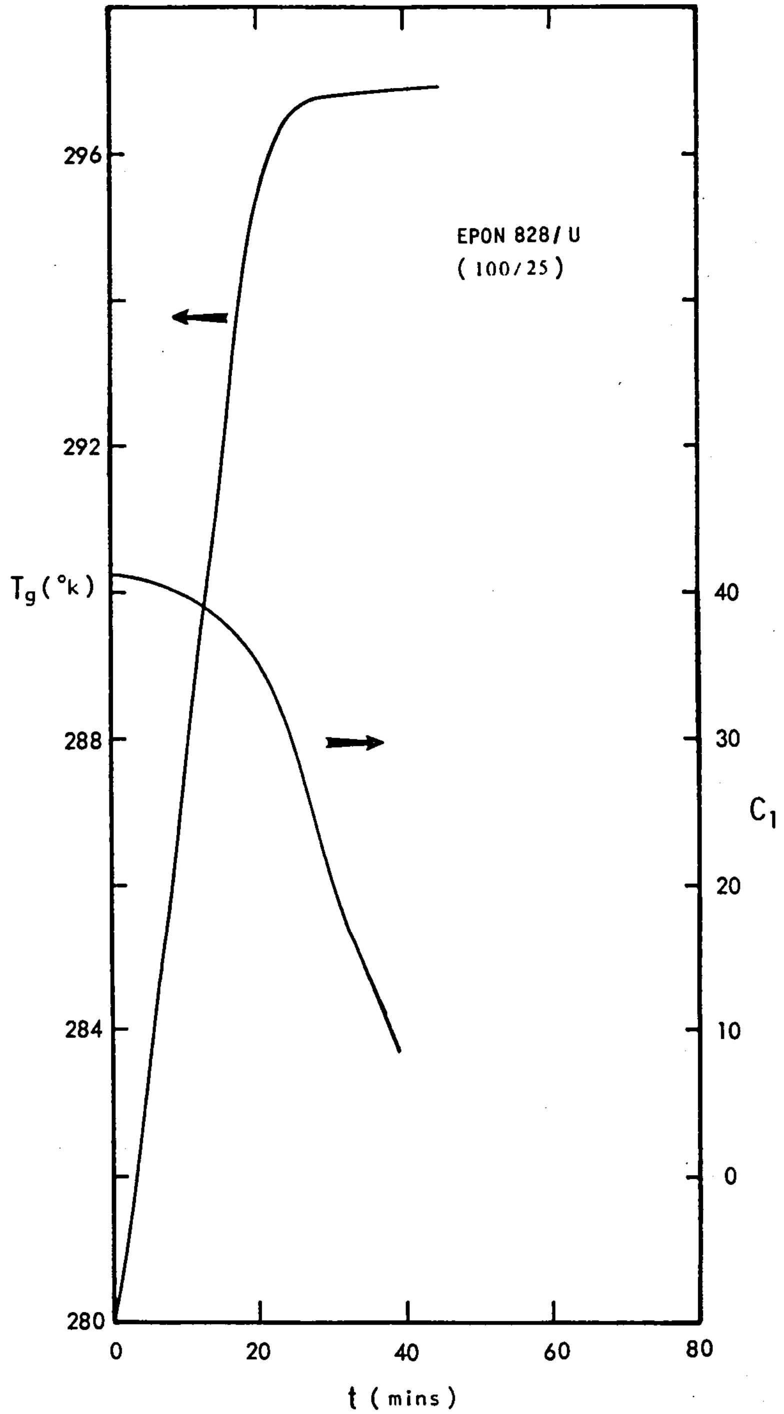

Figure 5. Variations of $T_g(t)$ and $C_1$ during cure obtained from the simulation model in Figure 2 for EPON 828/U resin system under dynamic heating conditions.

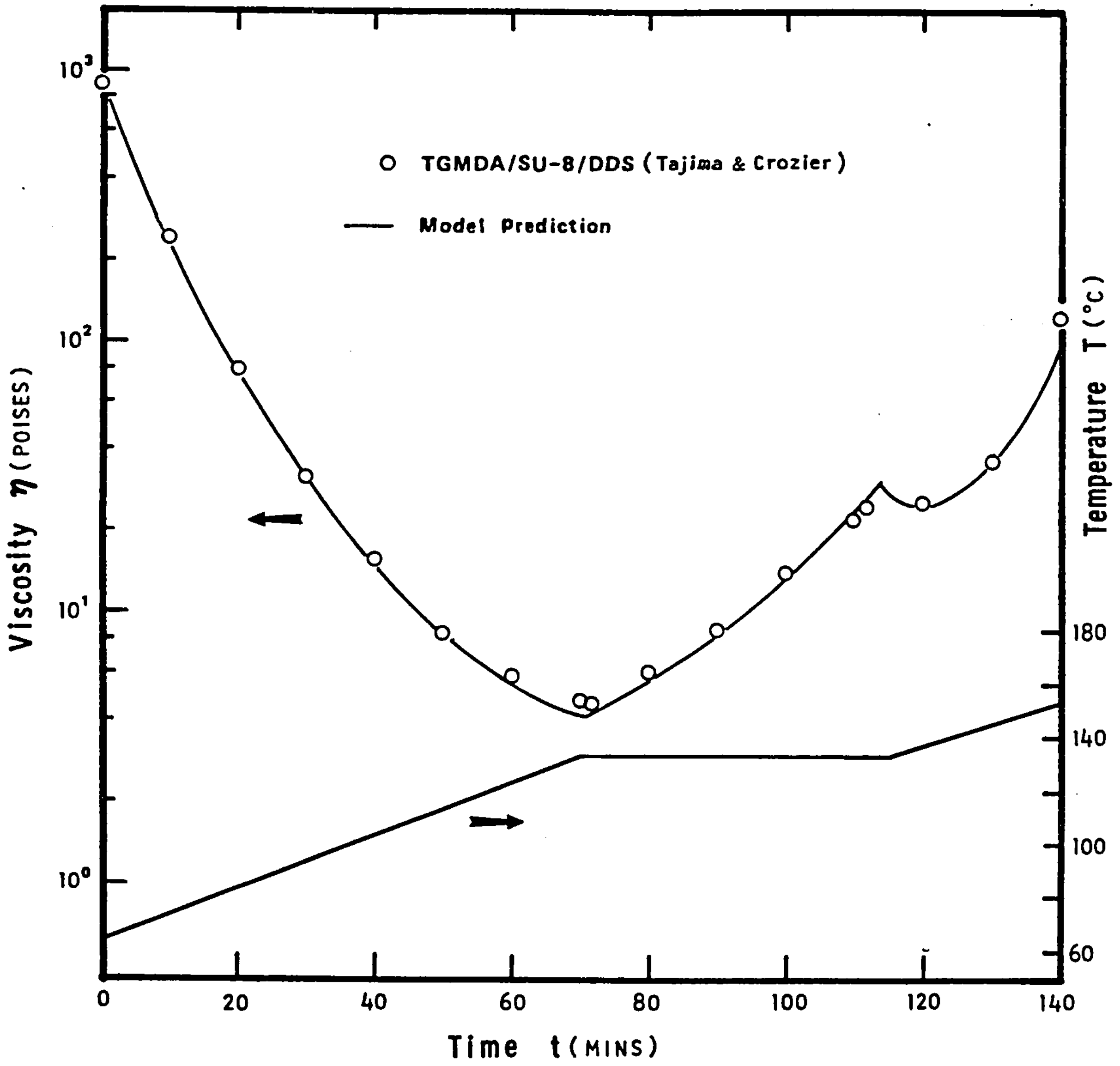

Figure 6. Comparisons between experimental non-isothermal chemoviscosity data and the model predictions. Cure cycle is also included. The data were reported by Tajima and Crozier for TGMDA-MY720/SU-8/DDS.

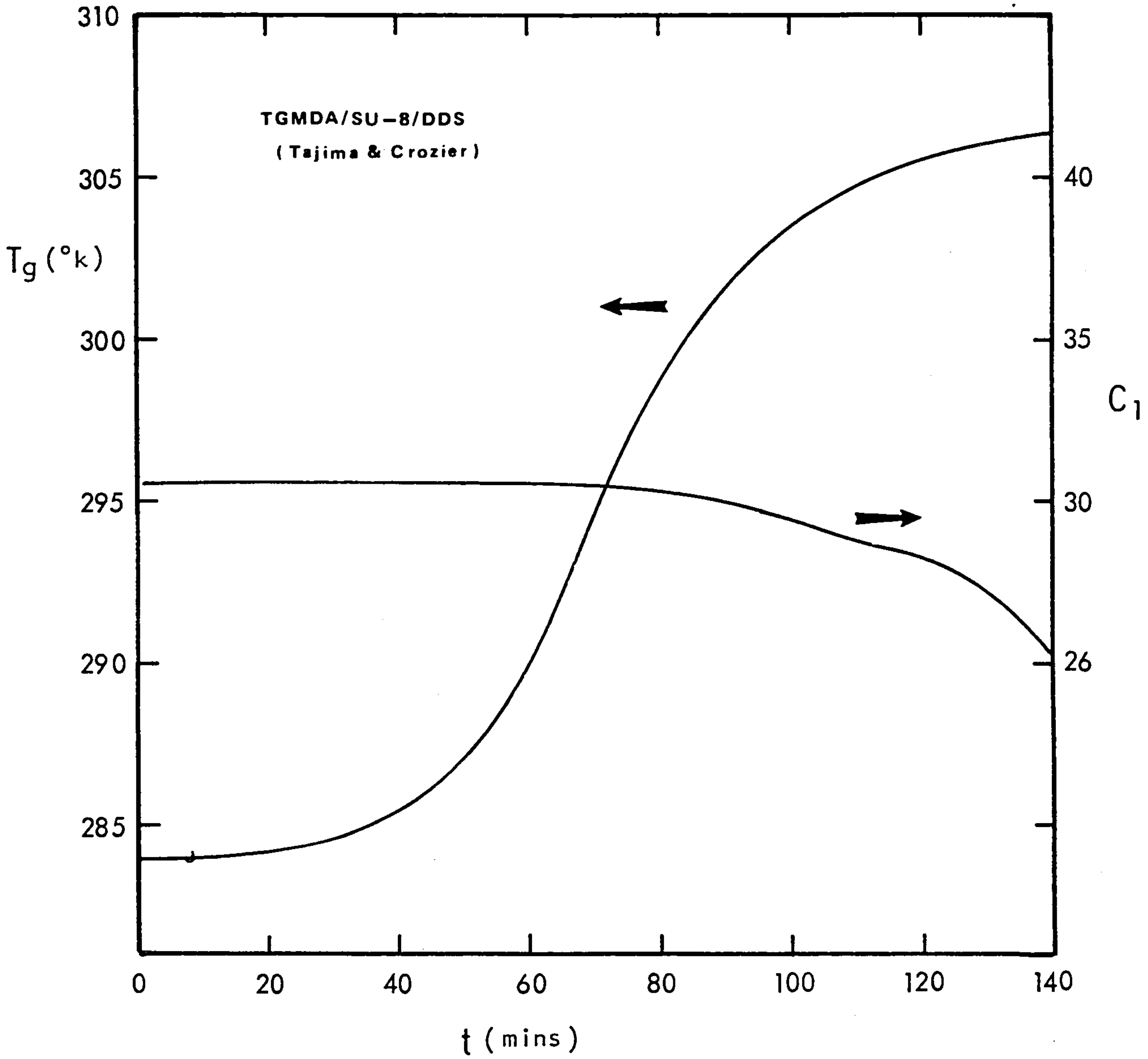

Figure 7. Variations of $T_g(t)$ and $C_1$ during cure obtained from the simulation model in Figure 6 for the TGMDA/SU-8/DDS resin system under dynamic heating conditions.

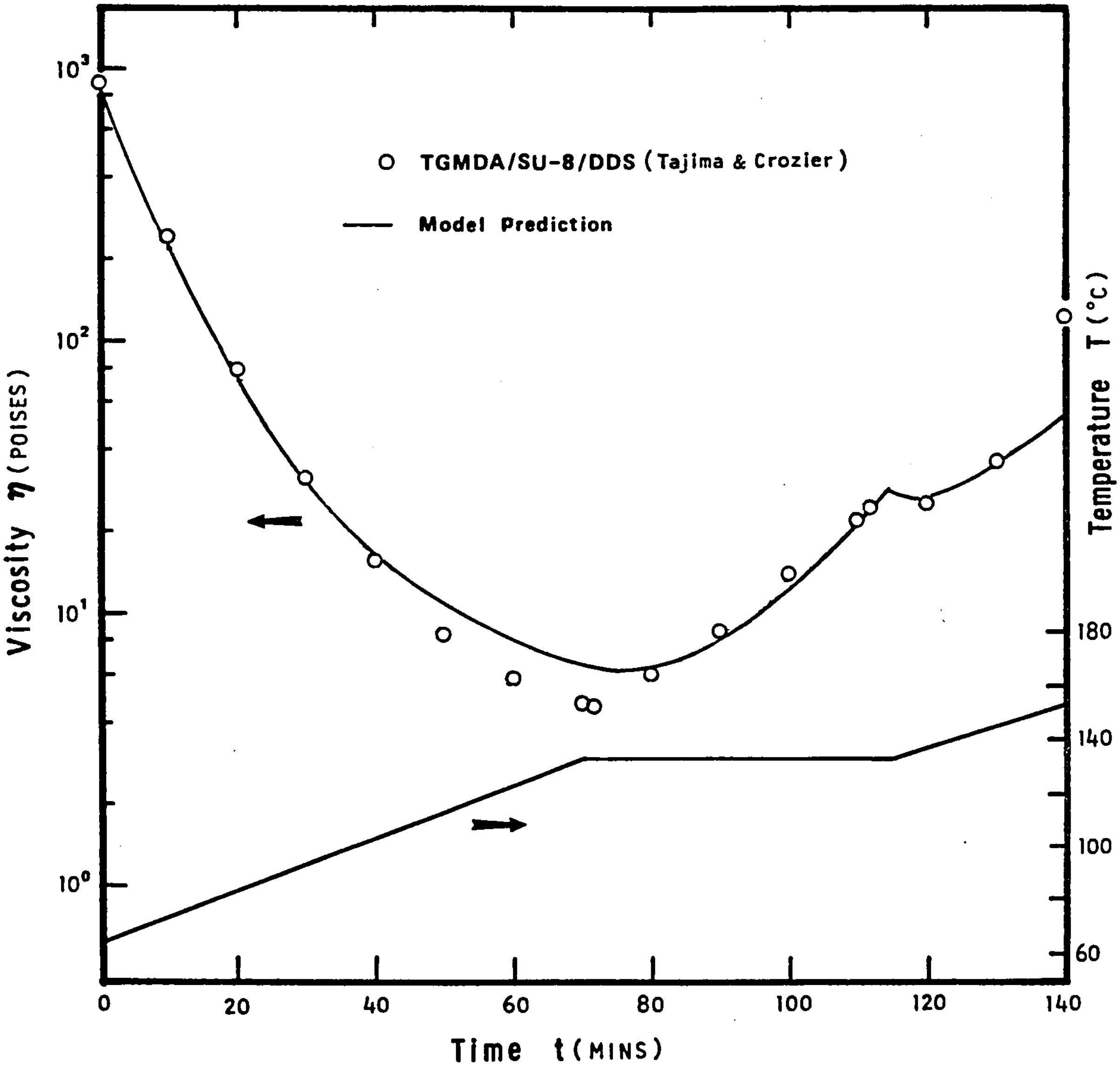

Figure 8. Same captions as in Figure 2, except that Eqs. (6a,b) are replaced by Eqs. (10a,b) to incorporate with the model Eq. (9).

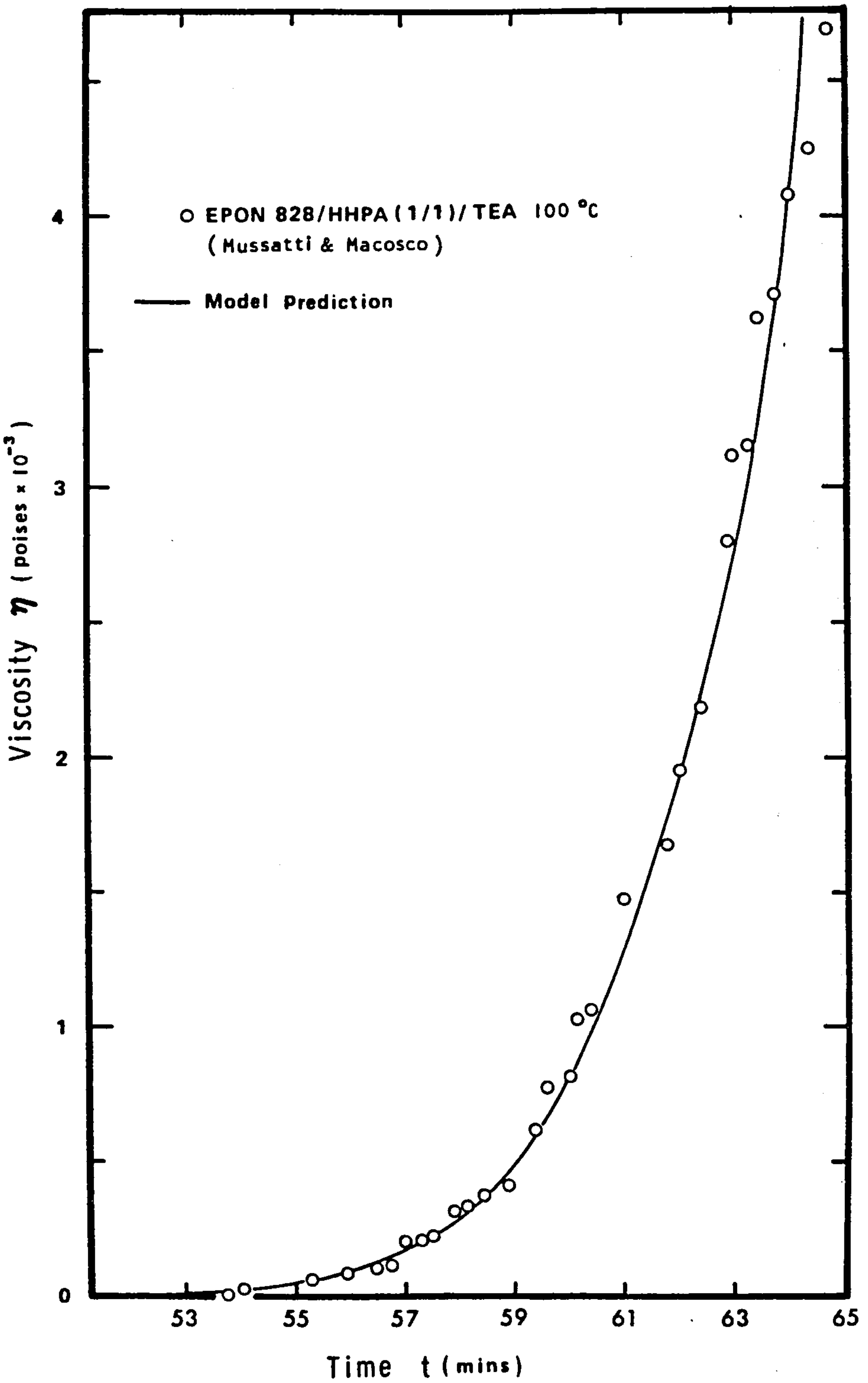

Figure 9. Comparisons between the experimental steady shear chemoviscosity data and the model predictions. Data were reported by Mussatti and Macosko for EPON 828/HHPA under isothermal curing at 100°C.

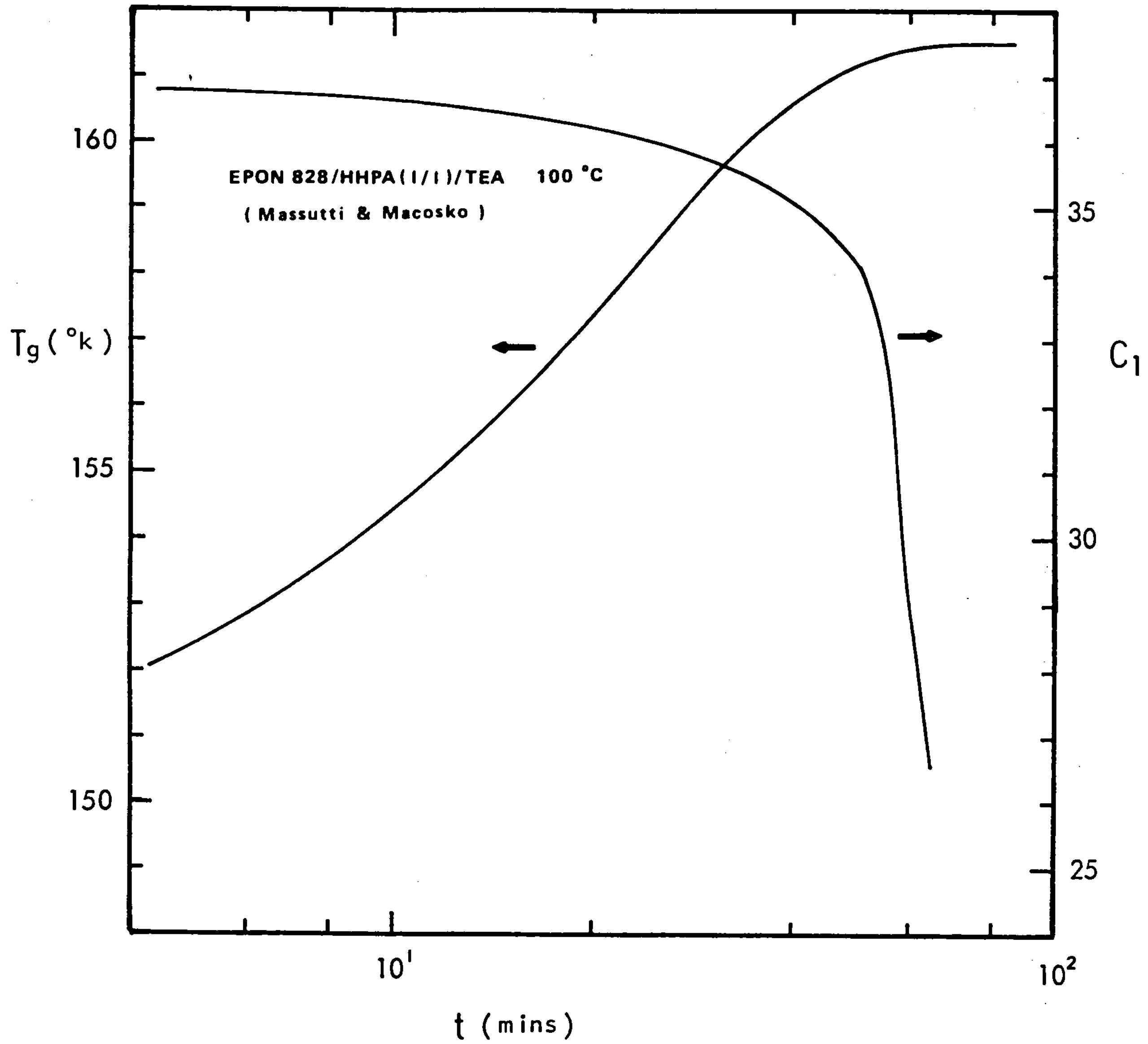

Figure 10. Variations of $T_g(t)$ and $C_1$ during cure obtained from the simulation model in Figure 9 for the EPON 828/HHPA/TEA resin system under isothermal cure conditions.

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16. Abstract

A new analytical model for chemoviscosity variation during cure of thermosetting resins has been developed. This model is derived by modifying the widely used WLF (Williams-Landel-Ferry) Theory in polymer rheology. Major assumptions involved are that the rate of reaction is diffusion controlled and is linearly inversely proportional to the viscosity of the medium over the entire cure cycle. The resultant first order nonlinear differential equation is solved numerically, and the model predictions compare favorably with experimental data of EPON 828/Agent U obtained on a Rheometrics System 4 Rheometer. It has been shown that the model can describe chemoviscosity up to a range of six orders of magnitude under isothermal curing conditions. The extremely non-linear chemoviscosity profile for a dynamic heating cure cycle can be predicted as well. The model is also shown to predict changes of glass transition temperature for the thermosetting resin during cure. The physical significance of this prediction is unclear at the present time, however, and further research is required. From the chemoviscosity simulation point of view, the technique of establishing an analytical model as described here can easily be applied to any thermosetting resin. The model thus obtained can be used in real-time process controls for fabricating composite materials.

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