Modelling the chemorheology of an epoxy resin system exhibiting complex curing behaviour

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Modified Williams–Landel–Ferry (WLF) equations were developed to calculate the chemoviscosity of an epoxy resin system exhibiting a complex curing reaction. The complex curing reaction of this resin was first resolved into three independent *n*th order reactions. The modified WLF equation can then be used to describe the chemoviscosity as a function of temperature and structural changes by allowing its parameters to vary with the changing structure of the curing resin. The structural dependence of the chemoviscosity is incorporated in the parameters of the modified WLF equation.

(Keywords: epoxy resin; complex cure kinetics; chemoviscosity; modified WLF equation)

INTRODUCTION

The most important aspect in the processing of thermosetting resins and fibre reinforced thermosetting resin matrix composites is the chemorheological behaviour of the resin. It is affected by the structural changes caused by the cure reaction and by variation in molecular mobility induced by changes in temperature[1]. The objective of a chemorheology model is to evaluate the chemoviscosity of the curing resin as a function of the prescribed cure cycle and cure kinetics of the resin. A chemorheology model includes two components: the reaction kinetics model, which predicts the reaction rate and degree of cure of the resin; and the chemoviscosity model, which relates viscosity to the degree of cure and temperature. These models, which are coupled to the temperature distribution model, govern various critical processing parameters[2].

Different approaches have been used to develop chemorheology models. Initial efforts to predict the chemoviscosity were to assume or experimentally derive a rate equation describing the change of viscosity with reaction time[3,4]. The temperature dependence of the kinetic parameters of this rate equation can then be expressed by the Arrhenius equation. In this approach, the chemoviscosity equation was essentially a fit of the measured viscosity to an exponential function of time which included empirical reaction rate parameters. It cannot be readily related to the chemistry of the curing resin system because it is not based on polymerization kinetics. Although sometimes useful[3,5], It is very much batch-specific and remains empirical in nature. Any chemoviscosity modelling must analytically include the effect of the structural change caused by the cure reaction.

Since the cure reaction directly controls the network structure of a thermoset, one of the recent approaches in modelling the chemoviscosity is to account for the network growth of the crosslinking polymer, and therefore the increase in viscosity, in terms of the change of the weight-average molecular weight during cure[6,7]. Reaction kinetics is utilized in branching theory to predict the structural parameters before and after the gel point. Once the structure of the network is established, it can be correlated with rheological properties.

Although fundamentally sound, the approach above is difficult to apply because the crosslinking mechanisms, which are essential in the calculation of network structure, are often difficult to identify for complex commercial epoxy resins. Another obstacle in applying this approach is that the kinetic analysis is difficult to perform for non-isothermal conditions due to a lack of understanding of the competitive reaction mechanisms taking place. Consequently, the chemoviscosity usually can only be calculated for isothermal conditions with model thermosetting resin networks.

An alternative approach of chemoviscosity modelling is to select an appropriate equation relating viscosity to temperature. The parameters of this equation are then expressed in terms of the reaction or reaction rate of the thermosetting resin. Several investigators have invoked the concept of free volume to calculate the changes in chemoviscosity[8–11]. Common to these studies is the use of various modified forms of the classical Williams–Landel–Ferry (WLF) equation. A modification of the WLF equation is necessary since the molecular structure of the curing resin is a function of the degree of cure, and therefore varies during the polymerization.

The purpose of this paper is to propose a chemoviscosity model based on the modified WLF equation for an epoxy resin widely used in the aerospace industry.

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A kinetic model for the cure reaction is also presented because any such chemoviscosity model cannot predict the viscosity variation unless there is an accurate kinetic expression that describes how the degree of cure may be predicted during reaction. These models have been compared successfully with experimental data.

EXPERIMENTAL

This study was carried out using the Hercules 3501-6 epoxy resin system. The standard formulation contains a major epoxide (tetraglycidyl methylenedianiline), two minor epoxides (alicyclic diepoxy carboxylate and epoxy cresol novalac), a hardener (diaminodiphenyl sulphone) and a Lewis acid catalyst (boron trifluoride monoethylamine complex)[12]. The material was provided by Bell Helicopter-Textron, and was stored in a freezer at 263 K until required. Before testing, the resin was degassed in a vacuum disiccator at room temperature for 24 h to remove any moisture which may deactivate the catalyst[13].

A Rheometrics mechanical spectrometer (model RMS-805) was used to measure the viscosity. Parallel plate geometry (25.4 or 50.8 mm in diameter) was used with gap sizes of 0.5–1 mm. The instrument was run in cure mode at two heating rates (1.25 and 2.5 K $\min^{-1}$) with a typical frequency of 1.59 Hz (10 rad s^{-1}) and strains of 5–20%. These values were chosen so that the resin samples remained Newtonian and linear viscoelastic[14]. Complex viscosity was measured; the Cox–Merz rule was proven to be applicable for a similar resin system[15], and it is assumed to be applicable here.

Measurements were performed on both the fresh and partially cured samples, which were also prepared in the RMS-805. The fresh sample was loaded into the warmed plates and held at constant temperature for various times. After conditioning, the resin was quenched with cold nitrogen gas. Small portions of the partially cured sample were then removed and scanned in a differential scanning calorimeter (Perkin-Elmer DSC-2) to measure the residual heat of reaction, which enabled the degree of cure to be determined.

Resin samples were also aged in the differential scanning calorimeter at different temperatures. After isothermal ageing, the sample was scanned at 5 K $\min^{-1}$ to determine the glass transition temperature (T_g) and residual heat of reaction. The T_g was taken as the midpoint of the deflection of the heat capacity change.

RESULTS AND DISCUSSION

Kinetic analysis

Details of the procedures used for kinetic analysis are discussed elsewhere[14]; only the important points and results are presented here. For the Hercules 3501-6 resin, the cure reaction is complex; there is more than one independent reaction during curing since three visible exothermic peaks can be observed on a dynamic d.s.c. scan, as shown in *Figure 1* for a heating rate of 5 K $\min^{-1}$. At higher heating rates, the reaction peak at the lowest temperature is less noticeable. In a dynamic d.s.c. scan, each exothermic peak represents an independent reaction[16]. The secondary reactions, which take place at lower temperatures, are introduced as flow modifiers; and they are related to the catalysed reactions[13]. The Hercules 3501-6 resin is a kinetically complex system, but it is often treated as a simple system.

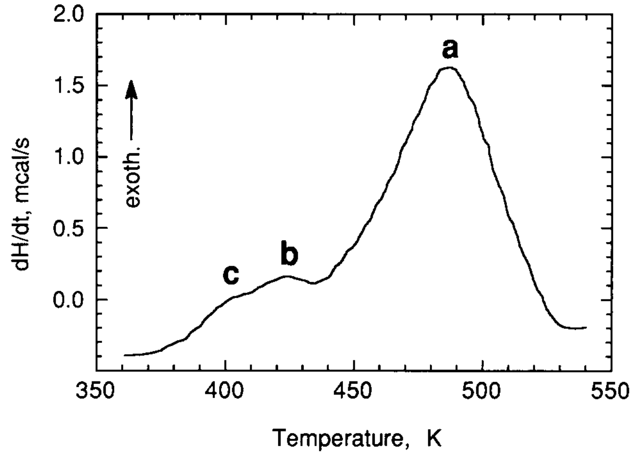

Figure 1 Digitized dynamic d.s.c. thermogram at a heating rate of 5 K $\min^{-1}$. Three reaction peaks can be observed in the temperature range of interest. Approximate positions of the reaction peaks: (a) major peak; (b) medium peak; (c) minor peak

Kinetic analysis of this resin system has employed isothermal methods[17]; however, complex reactions should not be treated with isothermal methods[16,18,19]. One reaction may dominate at some temperature; while others may dominate at other temperatures. The overall reaction rate is measured in isothermal d.s.c. measurements; and the contribution of individual reactions cannot be resolved. As a result, the complex curing reaction was often approximated by a single reaction[17].

Non-isothermal kinetic analysis can be used to overcome this problem. Due to the nature of complex reactions, however, the procedure is not straightforward. A combination method was necessary to characterize the complex resin system. The method used was based on an experimental technique suggested by Duswalt[20]. For a complex reaction consisting of independent reactions, one or more of the reactions can be forced to react to completion by ageing the sample at a suitable temperature. In the subsequent dynamic d.s.c. scan, only a single reaction peak remains so that suitable kinetic analysis may be performed. By repeating this procedure, each reaction peak can be resolved[14]. It should be noted that this technique is applicable only when the suitable reaction temperature is higher than the resin T_g, which can be identified during rescanning, otherwise the onset of diffusion control would complicate the analysis.

The complex curing reaction exhibited by the Hercules 3501-6 resin can be represented by three independent *n*th order reactions, and the overall reaction rate is a weighted sum of each reaction rate[14]:

$$\left.\frac{d\alpha}{dT}\right|_{\text{overall}} = \sum_{i=1}^{3} g_i \frac{A_i}{\beta} \exp\left(-\frac{E_i}{RT}\right)(1-\alpha_i)^{n_i} \qquad (1)$$

where E is the activation energy, A is the pre-exponential factor, $\beta(=dT/dt)$ is the heating rate, g is the weight factor and the sum of all gs is $1 . g_i = H_i/H_{\text{total}}$, where H_{total} is the total heat of reaction and H_i is the heat of reaction for each reaction peak. The temperature derivative is used on the left-hand side of equation (1) instead of the time derivative. The kinetic parameters obtained are listed in *Table 1*. From this table, the need to resolve each peak becomes evident. Since a different activation

Table 1 Kinetic parameters for the complex cure reaction of the Hercules 3501-6 resin

Peak	H ($\mathrm{J\,g^{-1}}$)	$\ln A$ ($\mathrm{s^{-1}}$)	E/R (K)	n	g
Major	427.8	17.37	11 220	1.06	0.850
Medium	50.0	19.16	10 250	1.17	0.095
Minor	27.4	46.22	20 570	3.05	0.055

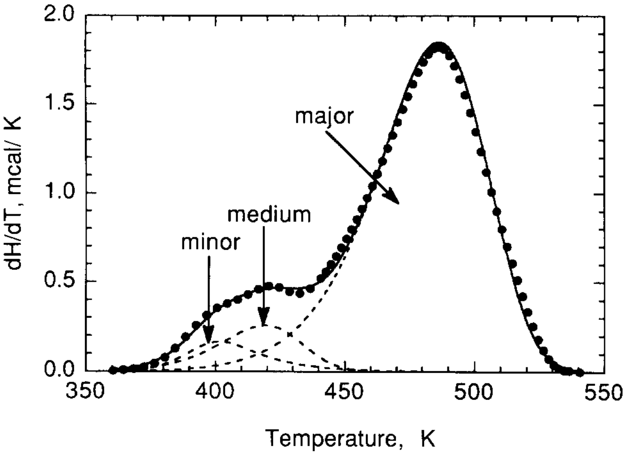

Figure 2 Comparison between the treated d.s.c. data (●) and the calculated result from equation (1) (——). Temperature derivative curves are shown. The overall reaction rate is a weighted sum of three reaction rates. The heating rate is $5\,\mathrm{K\,min^{-1}}$

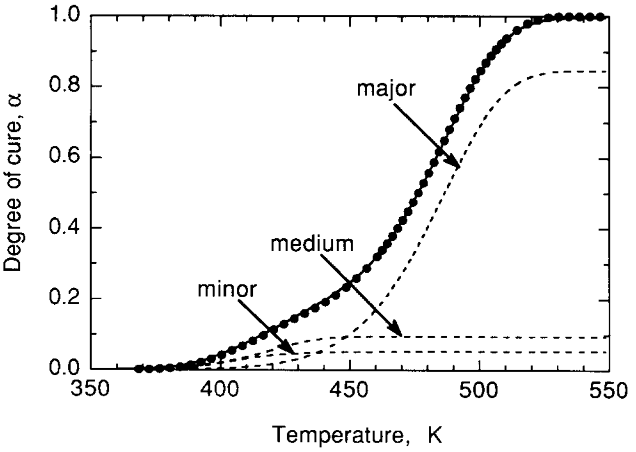

Figure 3 Comparison between the integral d.s.c. data (●) and the calculated result from the integration of equation (1) (——). The overall degree of cure is a weighted sum of those of three reactions

energy is associated with each reaction peak, the time–temperature characteristic of each peak is different. If a single reaction was used to approximate the complex reaction, the kinetic expression may suffer in general applicability.

The kinetic parameters obtained do not represent the actual crosslinking mechanisms. By representing the complex curing reaction with three thermal events, however, the cure kinetic can be successfully described. *Figure 2* shows the comparison between the experimental d.s.c. data at $5\,\mathrm{K\,min^{-1}}$ and the calculation based on the kinetic parameters listed in *Table 1*. The degree of cure *versus* temperature can be obtained by integrating equation (1); the comparison is shown in *Figure 3*.

Although the results presented in *Figures 2* and *3* are quite satisfactory, the kinetic equation was not applicable under isothermal conditions if the left-hand side of equation (1) was replaced by the time derivative, $d\alpha/dt$. The kinetic equation derived above underestimated the extent of cure as a function of time[14]. One possible reason is that the simple nth order reaction function might not have been general enough, and a better choice would be the autocatalytic reaction function, i.e. $f(\alpha)=\alpha^m(1-\alpha)^n$. The introduction of the additional kinetic parameter, however, would complicate the procedure of obtaining kinetic parameters into being an extremely difficult task. Another possible reason is that the dynamic kinetic equation simply cannot be used for the isothermal condition[1,14]. In any case, equation (1) can be used for dynamic conditions, and the calculations at other heating rates, though less accurate, are also satisfactory.

Chemoviscosity modelling

In 1955, Williams, Landel and Ferry expressed the variation of the viscosity of amorphous thermoplastic polymers with temperature between the glass transition and 100 K above the glass transition as[21]:

$$\ln\frac{\eta(T)}{\eta(T_g)}=\frac{-C_1(T-T_g)}{C_2+(T-T_g)} \tag{2}$$

where $\eta(T_g)$ is the viscosity at T_g; $\eta(T_g)$ is normally treated as a constant[22]. C_1 and C_2 are the material-dependent constants, but for any given polymer are not functions of temperature. C_1 and C_2 are related to f_g, the fractional free volume at the glass transition, and α_f, the coefficient of thermal expansion of the fractional free volume[21]. C_1 is identified with B/f_g and C_2 with f_g/α_f; and B is another material constant.

Unlike the thermoplastic polymers, for which the WLF equation was originally derived, thermosets undergo chemical reaction during cure, resulting in a continuous change of the polymer structure and a simultaneous increase in the T_g. Since the structure of the curing polymer is changing, it is also possible that C_1 and C_2 also vary as the network structure of the thermoset changes. Therefore, the classical WLF equation can be modified as:

$$\ln\frac{\eta(T)}{\eta(T_g)}=\frac{-C_1(\alpha)[T-T_g(\alpha)]}{C_2(\alpha)+[T-T_g(\alpha)]} \tag{3}$$

where α is the degree of cure. Since C_1 and C_2 vary with the changing structure of the polymer, they become parameters instead of constants. Similar modified forms of the WLF equation have also been suggested (to be discussed later).

The d.s.c. analysis can be used to determine the relationship between T_g and α. The T_g *versus* α data, as obtained on the differential scanning calorimeter from samples aged at four different temperatures for various times, are presented in *Figure 4*. Since the differential scanning calorimeter available is not equipped with low temperature capabilities, T_g can only be measured for $\alpha>0.4$. The T_g of the uncured resin available from the literature[10] is 283.94 K, which was obtained with a heating rate of $20\,\mathrm{K\,min^{-1}}$; this value is also included in the figure. DiBenedetto's equation[23] can be used to represent the relationship between T_g and α:

$$\frac{T_g-T_{g0}}{T_{g0}}=\frac{(\varepsilon_x/\varepsilon_m-F_x/F_m)\alpha}{1-(1-F_x/F_m)\alpha} \tag{4}$$

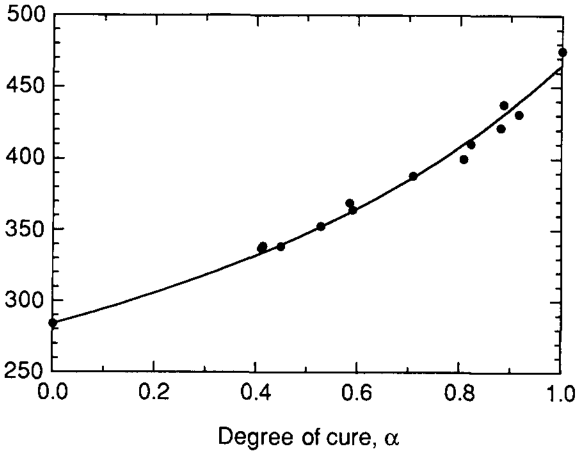

Figure 4 T_g as a function of the overall degree of cure: (●) experimental data obtained on a differential scanning calorimeter; (——) calculation from DiBenedetto's equation. The T_g of the uncured resin ($\alpha = 0$) was obtained from the literature

where T_{g0} is the glass transition of the uncrosslinked resin, $\varepsilon_x/\varepsilon_m$ is the ratio of lattice energies for the crosslinked and uncrosslinked polymers and F_x/F_m is the corresponding ratio of the segmental mobilities. In practice, the latter two parameters become curve fitting coefficients. For the data presented including the uncured resin's T_g of 283.94 K, $\varepsilon_x/\varepsilon_m = 0.887$ and $F_x/F_m = 0.541$; the result is plotted as the solid line in *Figure 4*. The T_g of the uncured resin used in this investigation was later measured on a separate differential scanning calorimeter as 280.5 K at 5 K min^{-1}, which was consistent with the heating rate used in the kinetic analysis. This value is 3.44 K lower than the literature value used above. The effect on the outcome of curve fitting is minimal (maximum error is 1.2% at T_{g0}), and the curve-fitting result above is used in the following analysis.

Since there are several reactions taking place at the same time and each reaction may be dominant at different temperatures, the network architecture should depend on the temperature histories. Therefore it is conceivable that the T_g *versus* α relationship is not unique for different temperature history. However, the T_gs presented in *Figure 4*, which were obtained from four different reaction temperatures (400, 425, 450 and 475 K), did not exhibit temperature history dependence. This is because these temperatures are high enough so that all the reactions are proceeding simultaneously.

The C_1 and C_2 *versus* α relationships can be obtained from the dynamic viscosity data. The viscosity *versus* temperature curves for the uncured and partially cured samples are shown in *Figure 5* for the heating rate of 2.5 K min^{-1}. For clarity, not all the data are shown. The degree of cure as determined by the d.s.c. analysis for each case before the viscosity measurement is listed. Only portions of the curve, in which the degree of cure is low so that the temperature change is the dominant effect, are shown.

Although there is always some cure reaction occurring in the temperature ranges shown in *Figure 5*, the effect of temperature change on the viscosity is much more dominant than the effect of the changing resin structure, as evident from the continuously decreasing trend exhibited by these viscosity curves. The state of the resin sample in these temperature ranges can be considered constant; and the decrease in viscosity can be considered solely due to the changes in temperature. The selection of the temperature range in which the effect of the temperature change dominates can be verified. *Figure 6* shows a comparison of the viscosity and calculated degree of cure curves for the uncured sample. It can be seen that the degree of cure is <5% in the corresponding temperature range of the viscosity curve shown in *Figure 5*. Typically, the region in which the temperature dominates is that before the minimum viscosity point.

To determine the relationships between the WLF parameters and degree of cure, the magnitude of the reference viscosity at the glass transition is first chosen as a constant of 10^9 Pa s, which was also used by other investigators[10]. The selection of the reference viscosity at the T_g is arbitrary here, but a different value will not affect the result of subsequent analysis. Since the state of the resin for each viscosity curve can be considered to be constant, the T_g associated with each viscosity curve can also be considered as a constant. The T_gs can be calculated from equation (4); and the C_1 and C_2 associated with each viscosity curve can be obtained from the slopes and intercepts of the plots of $(T - T_g)/\ln[\eta(T)/\eta(T_g)]$ *versus* $T - T_g$. The results are shown in *Figures 7* and *8*; and the relationships between C_1 and C_2 and the degree

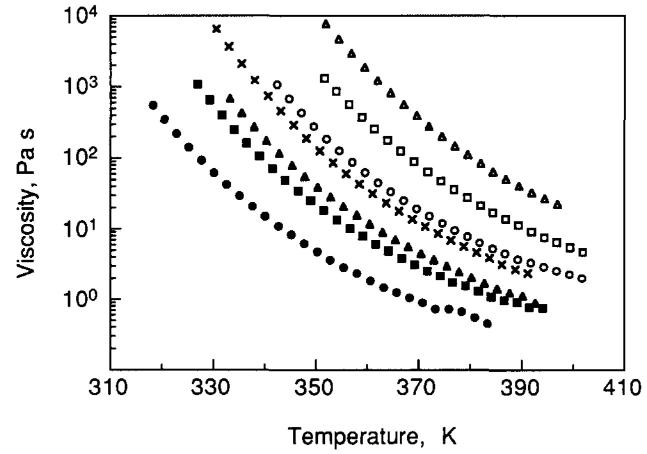

Figure 5 Viscosity curves for resin sample with various degrees of cure: (●) 0.0; (■) 0.055; (▲) 0.078; (×) 0.101; (○) 0.167; (□) 0.211; (△) 0.255. For clarity, not all the data are shown

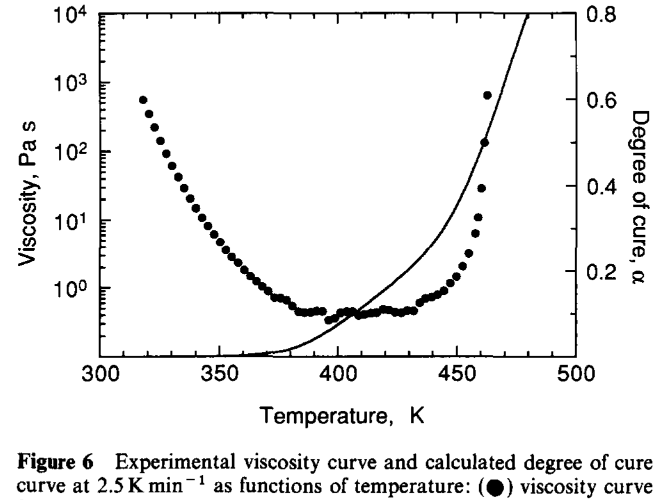

Figure 6 Experimental viscosity curve and calculated degree of cure curve at 2.5 K min^{-1} as functions of temperature: (●) viscosity curve for uncured resin; (——) calculated degree of cure curve. The degree of cure occurring between 320 K and 385 K is < 5%

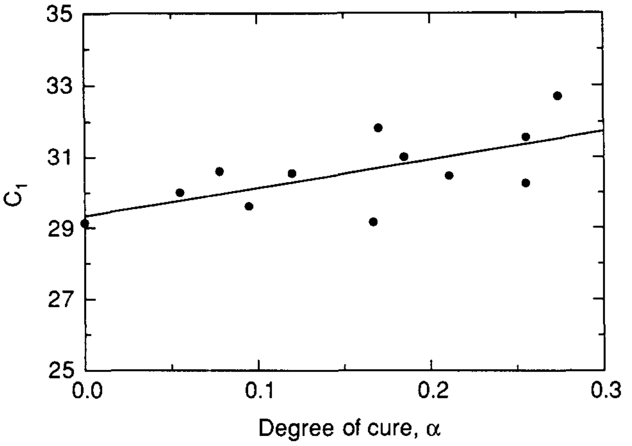

Figure 7 WLF parameter C_1 as a function of the degree of cure: (●) experimental data; (——) best-fit linear equation, $y=29.331+8.001x$

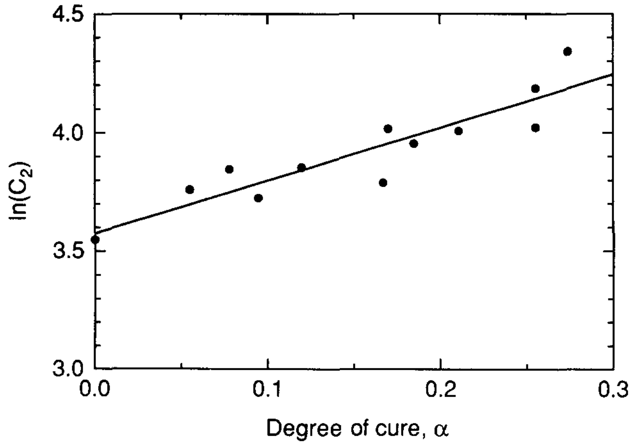

Figure 8 WLF parameter C_2 as a function of the degree of cure: (●) experimental data; (——) best-fit linear equation, $y=3.5731+2.2345x$

of cure are the best-fit linear equations:

$$C_1(\alpha)=29.331+8.0012\alpha \tag{5}$$

$$C_2(\alpha)=\exp(3.5731+2.2345\alpha) \tag{6}$$

With the equations above and DiBenedetto's equation as the T_g equation, all the equations needed to calculate the chemoviscosity for the curing of Hercules 3501-6 epoxy resin are now complete since the degree of cure can be calculated from the integration of equation (1). For the dynamic conditions of 1.25 and 2.5 K min^{-1}, the comparisons between the calculated chemoviscosity and experimental data are shown in *Figure 9*. In both cases, the results are satisfactory. Although equations (5) and (6) were established with data only for $\alpha<0.3$, the chemoviscosity calculation was able to follow the trend exhibited by the experimental data up to the gelation which occurs at $\alpha\approx0.58$. It should be noted, however, that the analysis presented above really does not predict the gel point. The analysis only approximates the gel point; the basis of the approximation is the systematic shifting of the viscosity curves from partially cured resin (*Figure 5*) and the resulting variation of C_1 and C_2 as a function of the degree of cure.

In the formulation above, both f_g and α_f were essentially allowed to vary with the changing structure of the curing resin. This is reasonable since the fractional free volume is related to the crosslink density. As the resin cures, both f_g and α_f decrease due to the increase in crosslink density. Although the magnitude of the reference viscosity at the glass transition is selected to be constant, one may argue that since the change in f_g is relatively small as reflected by the small dependence of C_1 on α shown in *Figure 7*, the change in $\eta(T_g)$ cannot be differentiated.

However, one may still argue that the constancy of the reference viscosity at the glass transition leads to the conclusion of iso-free volume at the glass transition. Consequently, f_g is constant, and C_1 should also be constant. Following this argument, the WLF equation can be modified as:

$$\ln\frac{\eta(T)}{\eta_{T_g0}}=\frac{-C_1[T-T_g(\alpha)]}{C_2(\alpha)+[T-T_g(\alpha)]} \tag{7}$$

where η_{T_g0} is the reference viscosity at the glass transition. If C_1 is indeed a constant, then the plot of $-C_1(T-T_g)/\ln[\eta(T)/\eta_{T_g0}]$ *versus* $T-T_g$ should be a straight line with a slope equal to 1 and an intercept equal to the value of C_2. In this formulation, the value of C_1 cannot be any constant but a constant that will lead to a slope of 1. The value of C_1 can be selected so that the resulting slopes of the plots of $-C_1(T-T_g)/\ln[\eta(T)/\eta_{T_g0}]$ *versus* $T-T_g$ are close to 1 for all the data. C_1 was selected to be 30.25; and the slopes of the resulting best-fit linear equations are within ±5% of 1. The values of C_2 can then be obtained from the intercepts; and the result is plotted as a function of the degree of cure in *Figure 10*.

In the case that C_1 is held constant at 30.25, the relationship between C_2 and the degree of cure is:

$$C_2(\alpha)=\exp(3.6251+1.7501\alpha) \tag{8}$$

The chemoviscosity can again be calculated; and the results for the heating rates of 1.25 and 2.5 K min^{-1} are shown in *Figure 11*, compared to the experimental data at the same heating rates. It can be seen that the chemoviscosity calculation in the case discussed above is also satisfactory.

The modified WLF equation suggested by Tajima and Crozier[8,24,25] has the form:

$$\ln\frac{\eta(T)}{\eta(T_{\mathrm{ref}})}=\frac{-C_1(T-T_{\mathrm{ref}})}{C_2+(T-T_{\mathrm{ref}})} \tag{9}$$

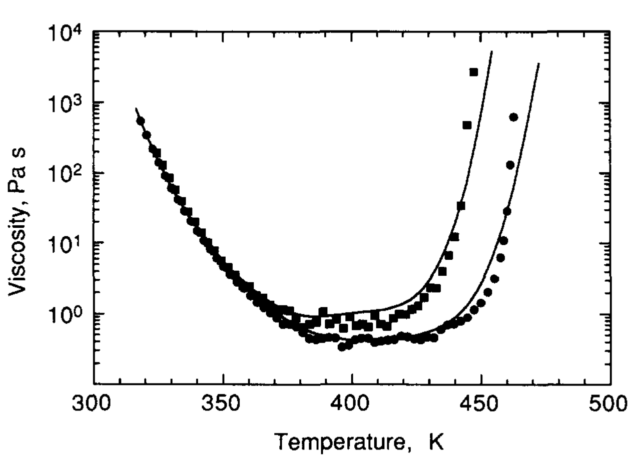

Figure 9 Comparisons between chemoviscosity data and calculations with varying C_1 and C_2: (●) experimental data at 2.5 K min^{-1}; (■) experimental data at 1.25 K min^{-1}; (——) chemoviscosity calculations at the corresponding heating rates

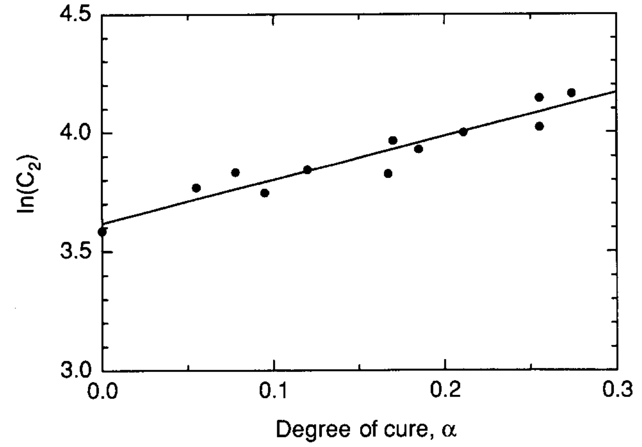

Figure 10 WLF parameter C_2 as a function of degree of cure when C_1 is constant: (●) experimental data; (——) best-fit linear equation, $y=3.6251+1.7501x$

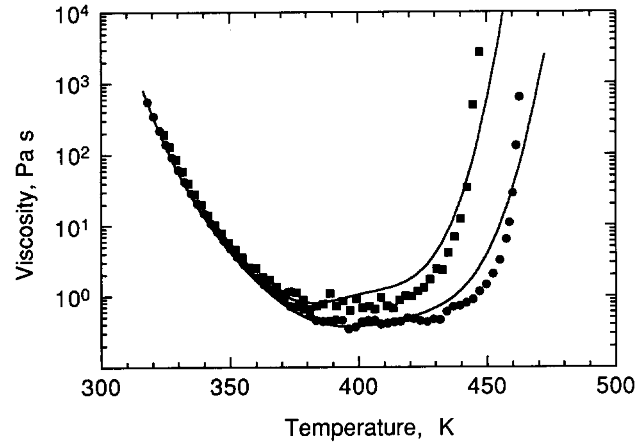

Figure 11 Comparisons between chemoviscosity data and calculations with varying C_2: (●) experimental data at 2.5 K min^{-1}; (■) experimental data at 1.25 K min^{-1}; (——) chemoviscosity calculations at the corresponding heating rates

where C_1 and C_2 are kept constant; and the effect of the cure state on viscosity can be considered by treating the reference temperature and reference viscosity as unknowns. It was used to investigate the chemorheology of the curing of a tetraglycidyl methylenedianiline/glycidyl ether novalac/diaminodiphenyl sulphone resin system[24] and a diglycidyl ether of bisphenol A/methylenedianiline resin system[25].

The procedures can also be applied to the data presented here. The viscosity curves shown in *Figure 5* can be shifted to construct the viscosity master curve. With the viscosity curve of zero initial degree of cure ($\alpha=0$) remaining in place, all the other curves with some degree of cure can be shifted in both the x and y directions so that a smooth master curve is obtained. The shifts on the x axis (temperature axis) and on the y axis (viscosity axis) needed for each curve to produce the smooth master curve can be used to determine the relationships between the reference temperature and reference viscosity and the cure kinetics of the resin[14].

In the procedures suggested by Tajima and Crozier[24,25], the reference temperature associated with the viscosity curve of zero degree cure was arbitrarily selected. The reference temperatures and reference viscosities obtained were then correlated with a kinetic parameter such as the rate of disappearance of the amine hardener. This method was extended to using the glass transition equation shown in equation (4); and the reference temperature and reference viscosity were correlated with the kinetic expression shown previously. The chemoviscosity calculation gives results similar to those shown in *Figures 9* and *11*[14].

The formulations discussed above are different from that proposed by Hou and Bai[10] and Mijovic and Lee[11], which were derived from isothermal viscosity data. In the procedure proposed by Mijovic and Lee, isothermal viscosity data were used to examine the chemoviscosity of diglycidyl ether of bisphenol A cured with methylenedianiline and *m*-phenylene diamine. The modified WLF equation was formulated as:

$$\ln\frac{\eta(T,t)}{\eta_{T_g0}}=\frac{-C_1(T)[T-T_g(\alpha)]}{C_2(T)+T-T_g(\alpha)} \tag{10}$$

where the reference viscosity, η_{T_g0}, is also considered to be a constant. An empirical relationship between T_g and α was employed. For each viscosity curve measured under isothermal conditions, C_1 and C_2 can be obtained by plotting $(T-T_g)/\ln[\eta(T,t)/\eta_{T_g0}]$ *versus* $T-T_g$.

Since isothermal viscosity data were used, the temperature T is constant for each isothermal viscosity curve, but T_g varies with the degree of cure or time. The logarithmic values of C_1 and C_2 obtained were then plotted as functions of $1/T$; and linear dependence was observed. The resulting modified WLF equation was successfully applied in calculating the chemoviscosity under isothermal conditions, but no data or calculation under dynamic conditions were presented. The same modified form of the WLF equation was also employed by Hou and Bai[10] in modelling the chemoviscosity of the same epoxy resin, i.e. the Hercules 3501-6 resin, used in this research. However, when the resulting C_1 and C_2 were plotted as functions of $1/T$, the dependence of C_1 and C_2 on $1/T$ was not systematic.

A possible source of error in Hou and Bai's investigation was that the degree of cure was not measured experimentally but calculated from a kinetic expression that is inaccurate. However, one may argue that the temperature dependence should be included in the form of the WLF equation, not in the WLF constants C_1 and C_2. It is reasonable for these constants to vary as functions of the resin structure when the epoxy resin cures since the structure is changing as the cure reaction proceeds. In addition, in the formulation of equation (10), the parameters C_1 and C_2 are not only functions of temperature but also functions of the structure since the resin structure is changing during an isothermal viscosity measurement.

It can be seen that the modified WLF equations proposed here can be used satisfactorily to predict the chemoviscosity at the heating rates of 1.25 and 2.5 K min^{-1}. Since no viscosity data were collected under higher heat rates, the applicability cannot be determined. However, slow heating rates are typical in many composite curing processes, and the results presented here are still useful, especially when the actual temperature inside a curing part is usually non-isothermal. As mentioned above, the kinetic equation was not applicable under isothermal conditions, but the modified WLF equations proposed here can still be used satisfactorily provided accurate degrees of cure are used in the calculation[14].

CONCLUSIONS

Modified WLF equations were developed to calculate the chemoviscosity of the Hercules 3501-6 epoxy resin system, which exhibits a complex curing reaction. The temperature dependence of the chemoviscosity is expressed in the formalism of the modified WLF equation. The structural dependence, on the other hand, is implicitly incorporated through the parameters of the modified WLF equation. The modified formulations proposed were consistent with the free volume argument. A prerequisite for the successful chemorheology modelling is an accurate kinetic expression. For the complex curing reaction of the Hercules 3501-6 resin, non-isothermal kinetic analysis may be used to characterize the cure kinetics. The theoretical predictions agree quite well with the experimental results.

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