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Steven H. Dillman^a; James C. Seferis^a

^a Polymeric Composites Laboratory Department of Chemical Engineering, University of Washington, Seattle, Washington

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KINETIC VISCOELASTICITY FOR THE DYNAMIC MECHANICAL PROPERTIES OF POLYMERIC SYSTEMS

STEVEN H. DILLMAN and JAMES C. SEFERIS*

Polymeric Composites Laboratory
Department of Chemical Engineering
University of Washington
Seattle, Washington 98195

ABSTRACT

A quantitative description for the dynamic mechanical properties of a reacting system as a function of both the viscoelastic and kinetic intrinsic behavior of the polymeric system was developed in this work. The model was tested experimentally by subjecting plaques of tetraglycidyl-4,4'-diaminodiphenylmethane partially cured with diaminodiphenyl sulfone to dynamic mechanical measurements at four isothermal temperatures. The kinetic viscoelasticity model was used to analyze the resulting data and to obtain both the characteristic intrinsic kinetic and viscoelastic parameters. The effects of temperature on the model parameters were investigated. Activation energies provided by the model for the curing reaction were found to agree with those obtained experimentally by other techniques. Experimental frequency was found to be an important factor in the kinetic analysis of dynamic mechanical data of curing systems. Finally, the analogy between dielectric relaxation and dynamic mechanical relaxation was found to be exploitable in developing modeling methodologies and analysis techniques applicable to both.

*To whom correspondence should be addressed.

INTRODUCTION

Dynamic mechanical analysis is commonly used in the characterization of polymeric materials. Considerable work has been performed in order to understand the viscoelastic behavior of nonreacting polymeric materials, and several models have been proposed to describe such behavior [1-5]. However, in many situations, such as the cure of composite parts, the structure, and therefore the viscoelastic behavior of the material, are changing with time. Several methods are available for describing the kinetics of reacting polymer systems [6, 7], and there have been several attempts to extract kinetic information from dynamic mechanical and ultrasonic data [8, 9]. However, no comprehensive model has yet been formulated that provides a complete description of the dynamic mechanical behavior of a curing material. Accordingly, this work provides a model describing the dynamic mechanical properties of reacting polymeric systems.

It is well known that the dynamic mechanical behavior of polymeric materials is strongly dependent on the frequency of oscillation [1, 2]. Models of reaction kinetics based on dynamic mechanical data have typically ignored the effects of test frequency, however. For this reason, kinetic parameters extracted from such models are frequency dependent and must be used with caution when applied to process description in the manufacture of polymeric parts.

In this work, viscoelastic and kinetic models are combined to form a viscoelastic model with time-dependent reaction parameters. The model is then demonstrated by describing isothermal dynamic mechanical data for a curing epoxy system consisting of tetraglycidyl-4,4'-diaminodiphenylmethane (TGDDM) epoxy cured with 35 parts per hundred diaminodiphenylsulfone (DDS). This is a model system which approximates a widely used high-performance matrix system for composites and whose kinetic behavior has been well characterized by other techniques [6, 7]. The effect of frequency and temperature on the model parameters and exhibited viscoelastic behavior of the model reacting polymeric system was investigated. Finally, implications toward extension of this development to nonisothermal conditions, described in detail in a separate communication, are also provided here for completeness [10].

EXPERIMENTAL

Samples used in this study were plaques made from a mixture consisting of TGDDM cured with 35 phr DDS. Mixing of the epoxy resin was performed

according to the procedure of Chu and Seferis as follows [11]: TGDDM and DDS were weighed out in the desired proportion. The TGDDM was placed in a beaker and heated in an oil bath to 135°C where it was held for 10 min. The DDS was then added slowly with vigorous mixing over a period of 10 min. Mixing continued for 10 min after the addition of DDS was complete. The resin was then removed from the oil bath, placed in a sealed glass container, and stored in a freezer at -10°C until used.

Prior to molding, the resin was degassed at 121°C under vacuum for 30 min. The resin was then poured into an aluminum mold which was lined with Du Pont Kapton film that had been coated with a release agent. The mold was then placed into an oven preheated to 177°C. The temperature of the oven dropped to about 135°C when the mold was placed into it and required about 35 min to return to 177°C. An additional 40 min of cure was required to obtain a gelled plaque.

The partially cured plaque was cut into 4 samples, each having dimensions of approximately 2.5 × 1.2 × 0.2 cm. Each sample was mounted in the horizontal clamp assembly of a Du Pont 982 dynamic mechanical analyzer (DMA) operating in conjunction with the Du Pont 1090 thermal analyzer.

The DMA had been calibrated according to the recommended procedures using the manufacturer's DMA calibration software. Calibration procedures included determination of: 1) the damping constant, a scaling parameter for the damping signal; 2) the instrument series compliance, a correction for error introduced by the compliance of the instrument; 3) the length correction factor, a parameter added to the sample length to account for clamping effects.

Dynamic mechanical tests were performed at four isothermal temperatures: 140, 167, 180, and 218°C. An oscillation amplitude of 0.2 mm was used. At this level, computed moduli are essentially independent of oscillation amplitude, implying that the sample behaves like a linearly viscoelastic material. In each case the sample was heated to the desired temperature at a rate of 20°C/min and held there until the complex modulus attained a constant value, indicating the completion of any detectable reaction.

Dynamic mechanical data are commonly expressed in several forms, all of which may be easily interrelated. Previously developed kinetic models for dynamic mechanical data have universally failed to provide a complete description of dynamic mechanical properties. For this reason it is necessary to provide a brief review of the methods of description of such properties.

The dynamic mechanical modulus, M^* , is defined as the ratio of an applied sinusoidal stress, σ^* , to the resulting sinusoidal strain, ϵ^* , in the material being tested. Typically, M^* is a complex quantity expressed as follows [12, 13]:

$$M^* = M' + iM'' = |M^*| e^{i\delta}, \quad (1)$$

$$|M^*|^2 = (M')^2 + (M'')^2, \quad (2)$$

$$\tan \delta = M''/M', \quad (3)$$

where M' = the storage modulus, a measure of the stress stored in the sample as mechanical energy

M'' = the loss modulus, a measure of the stress dissipated as heat

$|M^*|$ = the magnitude of the dynamic mechanical modulus

δ = the phase lag between the applied stress and the strain response

Thus, the dynamic mechanical modulus may be expressed by using either the storage and loss moduli, M' and M'' , or the magnitude and loss factor, $|M^*|$ and $\tan \delta$. Equations (1)–(3) apply regardless of whether the modulus in question is a tensile, shear, or flexural modulus, denoted E , G , and F , respectively.

In contrast, dynamic mechanical data may also be expressed in terms of complex compliance, J^* , defined as the reciprocal of the complex modulus [14]:

$$J^* = J' - iJ'' = |J^*| e^{-i\delta} = 1/M^*, \quad (4)$$

$$J' = M'/|M^*|, \quad (5)$$

$$J'' = M''/|M^*|, \quad (6)$$

$$|J^*|^2 = (J')^2 + (J'')^2 = 1/|M^*|^2, \quad (7)$$

$$\tan \delta = J''/J' = M''/M', \quad (8)$$

where J' = the storage compliance

J'' = the loss compliance

$|J^*|$ = the magnitude of the complex compliance

Thus, dynamic mechanical data may also be reported in terms of storage and loss compliances, J' and J'' , or compliance magnitude, $|J^*|$, and loss factor, $\tan \delta$. Equations (1)–(8) apply to moduli and compliances determined from any dynamic mechanical instrument, regardless of sample geometry [13].

Finally, dynamic mechanical data may also be expressed in terms of the complex dynamic viscosity, μ^* , most commonly in the case of "liquid" systems:

$$\mu^* = \mu' - i\mu'' = |\mu^*| e^{i(\delta - \pi/2)} = M^*/(i\omega), \quad (9)$$

$$\mu' = M''/\omega, \quad (10)$$

$$\mu'' = M'/\omega, \quad (11)$$

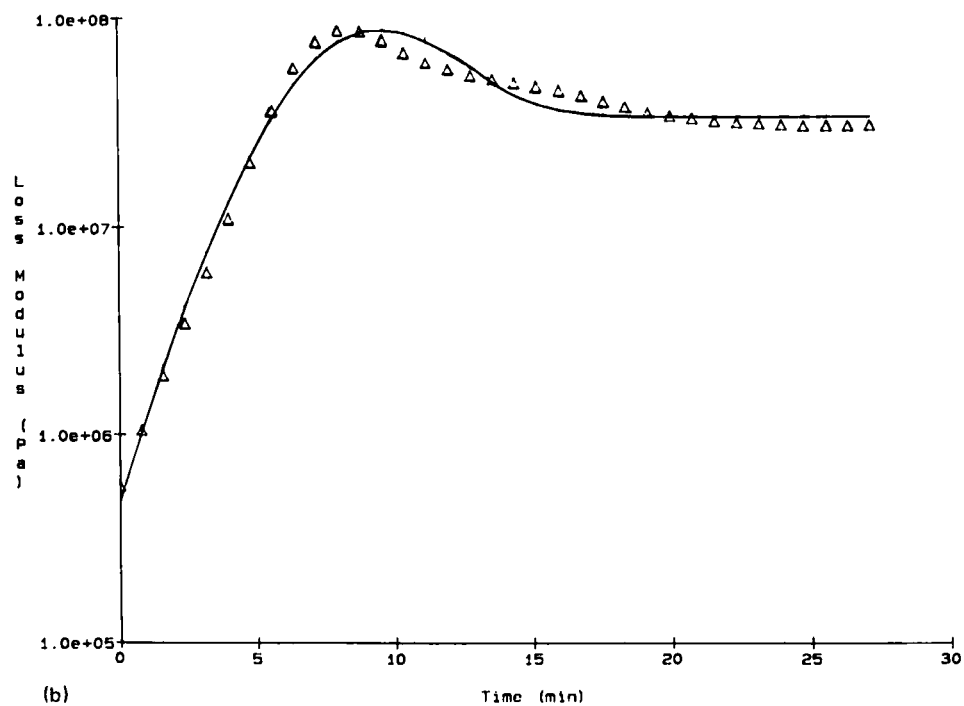
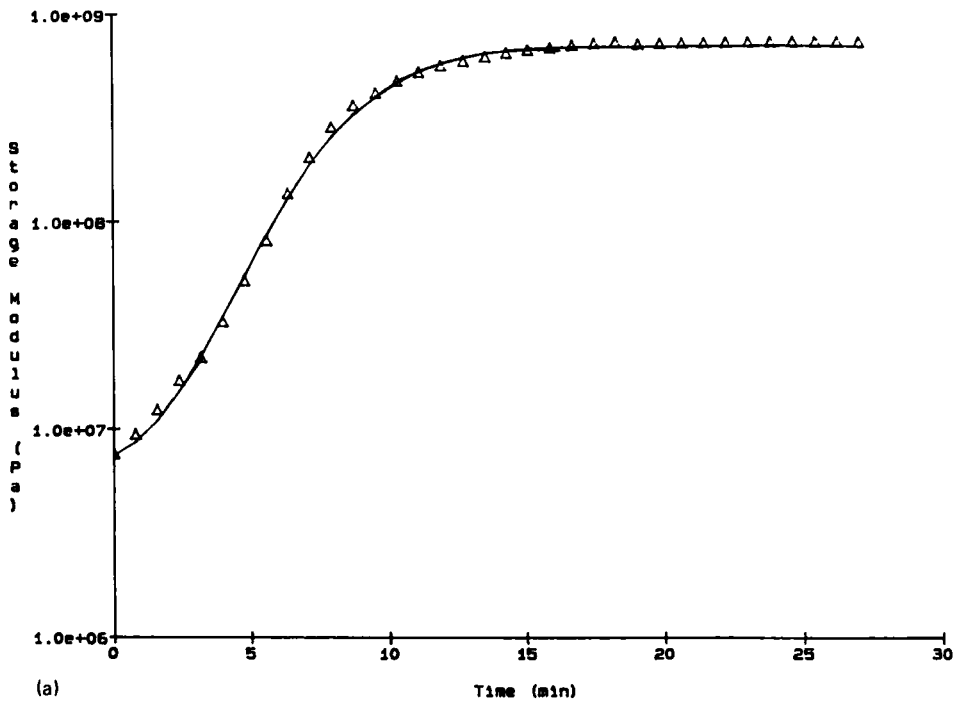
$$|\mu^*| = |M^*|/\omega. \quad (12)$$

It should be noted, however, that all of these methods of reporting data are equivalent. With knowledge of any two parameters, the others may be obtained by using the defining Eqs. (1)-(12). Therefore, a complete model must describe two quantities from which the others may be obtained.

RESULTS AND DISCUSSION

Typical plots of the storage and loss moduli of the TGDDM/DDS plaques as a function of time during an isothermal cure are given in Fig. 1. The storage modulus curve displays a sigmoidal shape while the loss modulus exhibits a peak followed by a decrease toward an asymptotic limit. This behavior, which has also been observed by other investigators during modulus measurements of curing epoxy systems, may be attributed to the hindering of molecular motions by crosslinks within the sample as it cures [15]. As the molecular motions become more restricted, the relaxation time of the sample increases. Similar behavior may be observed as a function of decreasing temperature, and therefore increasing relaxation time, for a nonreacting system [1, 2].

The mean relaxation time, τ , may be defined as the reciprocal of the frequency, ω , at the point where the loss modulus reaches a maximum. For a frequency scan of a nonreacting system, the mean relaxation time remains constant and the loss peak corresponds to the point where the frequency passes through $1/\tau$. For a temperature scan at constant frequency, the relaxation time decreases with increasing temperature and the loss peak corresponds to the point where $1/\tau$ passes through the frequency. This is equivalent to the time-temperature superposition concept [3]. In a curing system undergoing a variable-frequency experiment, both the frequency and the mean relaxation time are changing. However, the effect on the systems behavior can be viewed from within the same framework. As the sample cures, the relaxation time increases from a level such that $\omega\tau < 1$ to a value such that $\omega\tau > 1$, which gives rise to the observed peak in the loss modulus at $\omega\tau = 1$. To describe this behavior quantitatively, the kinetic effect of the cure reaction on the viscoelasticity of



the system must be determined. This is the intention of the model developed in this work.

Modeling Approach

Previous attempts to model dynamic mechanical behavior of curing systems have concentrated on describing one quantity, usually the storage modulus, M' , where two are required for a complete description. Typical studies on solid specimens focus on the storage modulus while ignoring the loss modulus, M'' [8, 9]. Studies of early cure generally focus on the magnitude of the dynamic viscosity, $|\mu^*|$, ignoring $\tan \delta$ [16]. However, a complete model must describe the behavior of two of these quantities from which the others may be calculated. This is accomplished through the use of a viscoelastic model as a foundation, accounting explicitly for both the frequency and temperature dependence of the material properties. The effect of cure is introduced by allowing appropriate parameters of the viscoelastic model to be functions of the cure kinetics of the system of interest. Thus, the key to the development of a successful model becomes the determination of an appropriate relationship between a viscoelastic model and a kinetic model.

This is similar to a constitutive approach taken in describing the complex dielectric constant and viscosity of curing thermosets [16, 17]. Viscoelastic and dielectric relaxation phenomena are analogous in many respects, including not only the analogous equations used in their description, but also with respect to the molecular origins of the motions which give rise to them [1, 18]. Table 1 provides an outline of the analogous description of dynamic mechanical and dielectric phenomena. This analogy is exploited here in the development of a dynamic mechanical model.

Viscoelastic Model

In general, the dynamic mechanical behavior of a nonreacting system is a function of the quantity $\omega\tau$, where ω is the measurement frequency and τ is the relaxation time of the system [1, 2]. The effect of temperature is accounted for by a decrease in the relaxation time with increasing temperature. For a polymer having a single relaxation, the dynamic mechanical properties as a function of $\omega\tau$ are as follows: at low values of $\omega\tau$ ($\ll 1$), the storage

FIG. 1. Dynamic mechanical shear modulus of curing TGDDM/35 phr DDS plaque at 218°C and resonant frequency. The solid line is the result of fit to model. (a) Storage modulus. (b) Loss modulus.

TABLE 1. Analogy between Dynamic Mechanical and Dielectric Phenomena

Dynamic mechanical	Fundamentals	Dielectric
Sinusoidal stress, σ^*	Driving force	Alternating electric field, E^*
Sinusoidal strain, ϵ^*	Response	Alternating electric polarization, D^*
$\epsilon^* = J^* \sigma^*$	Defining equation	$D^* = \epsilon^* E^*$
Complex compliance, $J^* = J' - iJ''$	Ratio of response to driving force	Complex dielectric constant, $\epsilon^* = \epsilon' - i\epsilon''$
	Single Relaxation Time Model	
Standard Linear Solid		Debye Relaxation
$J^* = J_u + (J_r - J_u)/(1 + i\omega\tau)$		$\epsilon^* = \epsilon_u + (\epsilon_r - \epsilon_u)/(1 + i\omega\tau)$
J_u = unrelaxed compliance		ϵ_u = unrelaxed dielectric constant
J_r = relaxed compliance		ϵ_r = relaxed dielectric constant
ω = stress frequency		ω = electric field frequency
τ = retardation time		τ = relaxation time

modulus is roughly constant at its minimum value, known as the relaxed modulus, and the loss modulus is small but increases with $\omega\tau$; at intermediate values of $\omega\tau$ (on the order of 1), the storage modulus increases rapidly with τ , and the loss modulus first increases rapidly, attains a maximum, and then decreases rapidly with $\omega\tau$; at large values of $\omega\tau$ ($\gg 1$), the storage modulus remains roughly constant at its maximum value, known as the unrelaxed modulus, and the loss modulus again becomes small and continues to decrease with increasing $\omega\tau$. The storage compliance behaves opposite to the storage modulus in that the relaxed compliance (low $\omega\tau$) is the maximum value and the unrelaxed compliance (high $\omega\tau$) is the minimum. The loss compliance behaves much the same as the loss modulus except that the transition region is at lower values of $\omega\tau$. The quantity τ may be defined based on the transition in compliance, in which case it is known as the retardation time.

The success of our dielectric model for curing systems using an analogous constitutive equation as well as the successful use of a similar relation in the modeling of viscoelastic behavior of a nonreacting system leads us to propose the following viscoelastic model as a constitutive relation for the description of dynamic mechanical data of both reacting and nonreacting systems [4, 17, 19]:

$$J^* = J' - iJ'' = J_u + (J_r - J_u)/[1 + (i\omega\tau)^\beta]^\alpha, \quad (13)$$

where J_u = the unrelaxed compliance

J_r = the relaxed compliance

ω = the experimental frequency

τ = the mean retardation time

β = a parameter ranging from 0 to 1 that accounts for a symmetric retardation time distribution

α = a parameter ranging from 0 to 1 that accounts for an asymmetric retardation time distribution

The relaxed compliance, J_r , represents the compliance of the material at low frequency or high temperature, when the sample is relatively flexible. The unrelaxed compliance, J_u , represents the compliance at high frequency or low temperature, when the sample is relatively stiff. The parameters α and β allow for the nonideality of the system by accounting for distributions of retardation times.

Several commonly used viscoelastic models are obtained from Eq. (13) by a suitable choice of parameters. If both α and β are set equal to 1, the model reduces to the Standard Linear Solid model, an ideal model with a single relax-

ation/retardation time, which has been used extensively in describing qualitatively the behavior of solid nonreacting systems [1, 2]. Further assumptions reduce the model to other viscoelastic functions. For example, if $J_u = 0$, one obtains the Voigt model [2]. Similarly, if the equation is expressed in terms of complex moduli and $G_r = 0$ (equivalent to $J_r = \infty$), the Maxwell model is obtained.

The real and imaginary terms of Eq. (13) can be easily separated, giving the following expressions:

$$J' = J_u + (J_r - J_u) \cos(\alpha\Theta) / [1 + 2(\omega\tau)^\beta \cos(\beta\pi/2) + (\omega\tau)^{2\beta}]^{1/2}, \quad (14)$$

$$J'' = (J_r - J_u) \sin(\alpha\Theta) / [1 + 2(\omega\tau)^\beta \cos(\beta\pi/2) + (\omega\tau)^{2\beta}]^{1/2}, \quad (15)$$

with

$$\tan \Theta = (\omega\tau)^\beta \sin(\beta\pi/2) / [1 + (\omega\tau)^\beta \cos(\beta\pi/2)]. \quad (16)$$

The general applicability of an expression such as this to dynamic mechanical data of nonreacting polymeric materials has been previously demonstrated [4]. However, for reacting systems, a description of the kinetics of the system and their effects on the viscoelastic model are required before a complete description is provided.

Kinetic Model

A variety of kinetic models may be utilized in describing the curing process of thermosetting systems [6, 7, 20]. The kinetics of the TGDDM/DDS epoxy system have in particular been successfully examined using n th-order kinetics accounting for the different reacting regions [6]. Accordingly, n th-order kinetics will be used in the development presented here. However, it should be noted that any appropriate kinetic expression may be used to describe a given system. The differential equation describing n th-order kinetics is

$$dX/dt = k(1 - X)^n, \quad (17)$$

where X = the dimensionless extent of reaction

k = the rate constant

n = the reaction order

Defining $X = 0$ at $t = 0$ gives the following integrated form of Eq. (17):

$$n = 1: \quad \ln(1 - X) = -kt, \quad (18)$$

$$n \neq 1: \quad \ln(1 - X) = [1/(1 - n)] \ln [1 + (n - 1)kt]. \quad (19)$$

This kinetic model may be used to describe the state of cure of the sample as a function of time. Thus, for the model development, the relationship between the state of cure and the viscoelastic behavior must now be provided.

Relating Kinetic and Viscoelastic Models

In order to predict the viscoelastic behavior of the sample as a function of time, the appropriate kinetic model must be incorporated into the viscoelastic model. The viscoelastic model contains five parameters which may be dependent on the extent of reaction in the system: J_r , J_u , α , β , and τ . The unrelaxed modulus and, hence, the unrelaxed compliance do not appear to change significantly after gelation; therefore, it will be assumed constant.

For systems which undergo significant chemical change during crosslinking, such as the epoxy system of this study, the retardation time increases with degree of cure [21]. According to rubber elasticity theory, the relaxed modulus, and thus the reciprocal of the relaxed compliance, should be linearly dependent on the crosslink density. However, the effect of changes in the relaxed compliance are small relative to the effect of changes in the retardation time except when the sample is relaxed. A state of relaxation is never achieved, however, since the sample resumes curing before its compliance nears the relaxed value. For this reason, J_r may be assumed constant to a first approximation. It must be noted that this assumption is invalid for systems that do not experience large changes in relaxation/retardation times during cure.

For simplicity, α and β will also be assumed independent of the state of cure. Although these assumptions cannot be expected to be observed in general, the effect of cure on the retardation time, τ , may be large enough to render changes in the other parameters insignificant. This approach is justified empirically by the success of a similar approach in describing dielectric behavior of reacting systems [17].

With these assumptions, only one parameter, the retardation time, remains to be described kinetically. The approach taken here is based upon our previous work in the development of a viscosity model for curing thermosets prior to the gel point [16]. Based on molecular weight considerations, the following expression for n th-order kinetics was obtained:

$$\ln \mu = \ln \mu_0 + [\Phi/(n - 1)] \ln [1 + (n - 1)kt], \quad (20)$$

where μ = the viscosity of the curing system

μ_0 = the initial viscosity

Φ = a parameter accounting for the effects of chain entanglement

From Eqs. (19) and (20), it can be seen that this is equivalent to

$$\mu_0/\mu = (1 - X)^\Phi. \quad (21)$$

Using these expressions and assuming proportionality between viscosity and retardation time leads to the following expressions:

$$\ln \tau = \ln \tau_0 + [\Phi/(n - 1)] \ln [1 + (n - 1)kt], \quad (22)$$

$$\tau_0/\tau = (1 - X)^\Phi, \quad (23)$$

where τ = the mean retardation time

τ_0 = the mean retardation time at $t = 0$

It should be noted that Eq. (22) should not be used for modeling postgelation dynamic mechanical data because it predicts a retardation time which increases without bound, while dynamic mechanical data show an asymptotic limit, here denoted as τ_∞ . However, a full cure limit to the retardation time may be introduced by assuming that the material behaves as a composite of cured and uncured regions, and that it obeys a series addition approximation, a common assumption for heterogeneous systems [5, 11]. With these assumptions, Eq. (22) may be expanded in the following way:

$$1/\tau = (1 - X')/\tau_\infty + X'/\tau_0, \quad (24)$$

where

$$X' = (1 - X)^\Phi. \quad (25)$$

This leads to the following expression:

$$(1/\tau - 1/\tau_\infty)/(1/\tau_0 - 1/\tau_\infty) = (1 - X)^\Phi. \quad (26)$$

It should be noted that this expression reduces to Eq. (23) when $\tau_\infty = \infty$.

When Eqs. (26) and (19) are combined, a generalized expression for the retardation time as a function of time is obtained:

$$\ln [(1/\tau_0 - 1/\tau_\infty)/(1/\tau - 1/\tau_\infty)] = [\Phi/(n - 1)] \ln [1 + (n - 1)kt]. \quad (27)$$

If the parameters are known, τ , at any given time, may be computed from Eq. (27). Once τ is known, the complex compliance may be computed from Eqs. (13) through (16). This requires knowledge of nine parameters in the general case: J_u , J_r , τ_0 , τ_∞ , α , β , Φ , n , and k , of which Φ , n , and k are inseparable for the isothermal experiments. In practice, J_r , J_u , τ_∞ , and possibly α and β may be determined from dynamic experiments on fully cured samples.

Analysis of DMA Data

As was mentioned previously, the DMA data were taken with a Du Pont 982 DMA. Because this instrument operates at resonant frequency, kinetic analysis techniques which rely on the time at which a given feature in the dynamic mechanical data is observed are prone to error introduced by changes in frequency between experiments and within the same experiment. The model presented here accounts explicitly for frequency, and therefore, may be applied to resonant as well as constant frequency data. Application of the model to resonant frequency data is somewhat more difficult, however, because the frequency is dependent on the modulus, making the calculations iterative.

The TGDDM/DDS system shows multiple relaxations. However, in the temperature and frequency range of the data taken in this work, only one transition, the α transition, has a significant effect. For this reason, the other transitions have been ignored.

A nonlinear least-squares data-fitting scheme based upon the path of steepest descent method was used to fit the model to the isothermal dynamic mechanical data [22]. The sum of errors in the storage and loss compliance was used as the objective function. A comparison of the model to the data at 220°C is given in Fig. 1. The parameters giving the best fit are given in Table 2.

The parameters shown in Table 2 exhibit some interesting trends with temperature. An analysis of the temperature dependence of the parameters is provided in the nonisothermal extension of the model [10]. However, the influence of temperature on the parameters is examined here.

The reaction rate constant, $(n - 1)k$, appears to vary exponentially with temperature. If an Arrhenius dependence is assumed, the natural logarithm of the rate constant should vary linearly with reciprocal temperature. However, here the rate constant is correlated strongly with the chain entanglement parameter, $\Phi/(n - 1)$. Thus, it is difficult to separate their effects during

TABLE 2. Model Parameters Generated by Minimization of Error in Storage and Loss Moduli

Parameter	Temperature, °C			
	140	167	180	218
$(n - 1)k, \text{min}^{-1}$	6.25E-3	8.19E-3	1.06E-1	1.45E-1
$\Phi/(n - 1)$	22.5	46.6	12.3	24.9
α	0.487	0.758	1.00	1.00
β	0.594	0.497	0.375	0.280
τ_0, s	8.71E2	8.87E0	7.74E-3	2.67E-4
τ_∞, s	1.30E7	5.69E6	1.05E8	8.29E8
J_r, Pa^{-1} : Average value = 2.76E-7				
J_u, Pa^{-1} : Average value = 1.26E-9				

the minimization process, particularly if n is close to 1. For this reason, it was determined that the quantity Φk was less subject to randomness. An Arrhenius plot was constructed using $\ln(\Phi k)$ as a function of $1/T$ (Fig. 2). The plot appears linear with some scatter, again due to the problem of separating the effects of Φ and k . The slope yields an activation energy of 17.3 kcal/mol. Table 3 gives apparent activation energies for the TGDDM/DDS system obtained by this technique as well as differential scanning calorimetry and dielectric analysis. The value obtained here agrees favorably with those obtained using other techniques.

The parameter α appears to increase with temperature, reaching its upper limit of 1.0 at roughly 180°C, and β appears to decrease with temperature. While the functionality of these changes is difficult to determine, it is suggested that, as a first approximation, α and β may be suitably modeled by a linear function of temperature with appropriate bounds.

The initial retardation time, τ_0 , decreases with increasing temperature. If Andrade (Arrhenius type) behavior is valid, the initial retardation time should vary exponentially with reciprocal temperature [1, 23]. An Arrhenius plot of the initial retardation time is shown in Fig. 3. The data appear linear, indicating that for this system the temperature dependence of the retardation time may be modeled, in this case, by the Andrade equation. For other systems a more complex approach, such as that of Williams, Landel, and Ferry,

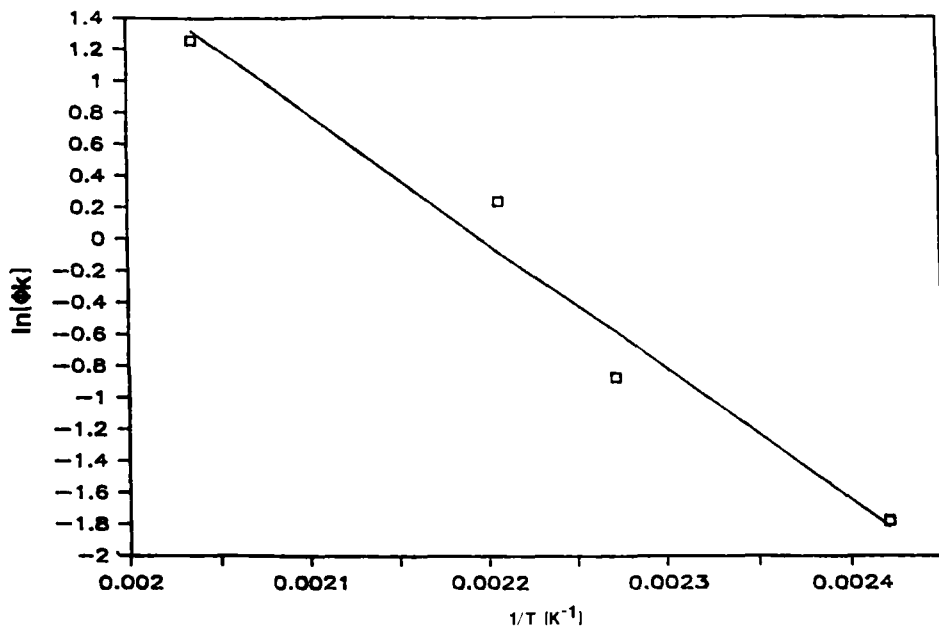


FIG. 2. Arrhenius plot of $\ln(\Phi k)$ as a function of $1/T$ for TGDDM/35 phr DDS based on model fit of data at 140, 167, 180, and 218°C. The slope of the solid line yields an activation energy of 17.3 kcal/mol.

TABLE 3. Apparent Activation Energies (TGDDM/35 phr DDS)

Technique	E_a , kcal/mol
Dynamic mechanical analysis	17.3
Differential scanning calorimetry [6]	16.7
Dielectric [17]	12-13

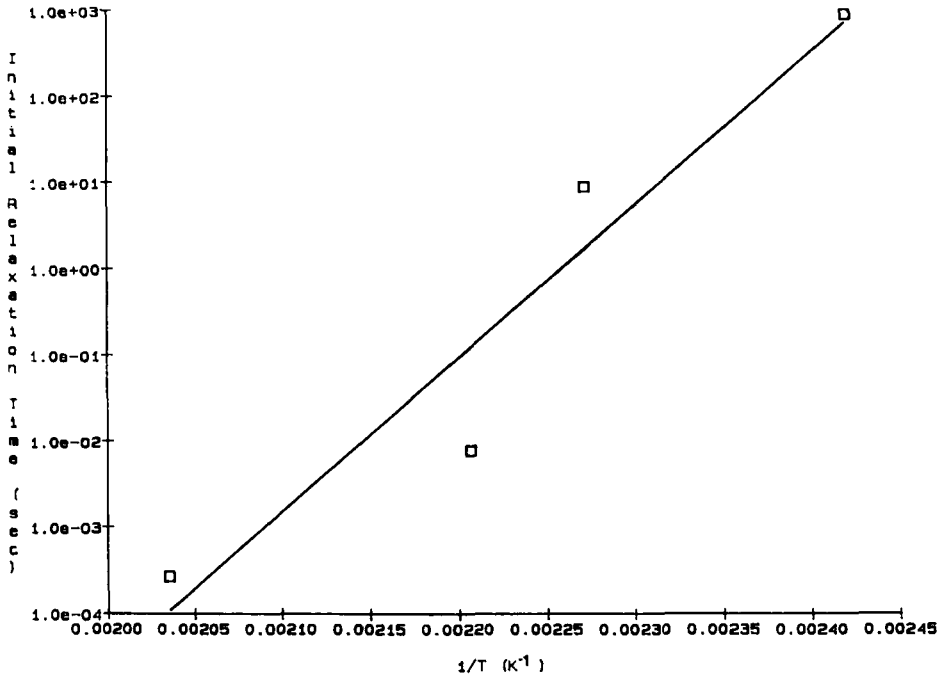


FIG. 3. Arrhenius plot of $\ln(\tau_0)$ as a function of $1/T$ for TGDDM/35 phr DDS sample.

may be required to account for the temperature dependence of the initial retardation time [3].

The final retardation time, τ_∞ , shows complex temperature behavior. It initially decreases with temperature followed by an increase with temperature. This can be explained by recalling that the final degree of cure attained is dependent on cure temperature [24]. Thus, there are competing effects: a tendency for retardation time to decrease with increasing temperature at a given state of cure, and the tendency for the system to reach a higher degree of cure at higher temperatures, increasing the retardation time.

Neither the relaxed nor the unrelaxed compliance shows any trends with temperature beyond apparent scatter of the data. Rubberlike elasticity theory predicts a decrease in the relaxed compliance with increasing temperature, but this effect is small over the range of temperature and compliance covered by

the data. Thus, both the relaxed and unrelaxed compliances may be assumed to be temperature independent within the accuracy of the model.

Predicted Frequency Effects

Once the model parameters had been determined, the model was used to predict frequency effects on the results of dynamic mechanical tests during cure. Plots of the effects on storage and loss moduli are shown in Fig. 4. It should be noted that the final value of the storage modulus increases with frequency and that the position of the loss peak shifts to earlier times with increasing frequency. As can be seen, if these predictions approximate a real system, failure to account for frequency effects when analyzing dynamic mechanical data for kinetic parameters could result in serious error.

Cole-Cole Type Plots

Since Eqs. (14)-(17) are parametric equations in τ , a plot of J'' vs J' will fall on a single curve, irrespective of frequency. Varying the frequency only varies the position along the curve observed for a given retardation time. Similar plots are commonly used in the analysis of dielectric data and are known as Cole-Cole plots [1]. Recently Cole-Cole plots have been shown to be effective tools in the analysis of dynamic mechanical data [25]. A typical Cole-Cole type plot for the isothermal data is shown in Fig. 5. If α , β , J_u , and J_r are independent of temperature, then the J'' vs J' curve should be independent of temperature also. Unfortunately, α and β are strongly temperature dependent, which results in a family of curves. However, useful information may be extracted from the plots of J'' vs J' . For example, the parameters α , β , J_u , and J_r may be extracted from the Cole-Cole type plot by using graphical or numerical techniques [17]. Table 4 gives parameters obtained from least-squares analysis of the Cole-Cole plots. α , β , and J_u agree well with the parameters in Table 2 obtained by numerical analysis of the data. J_r , however, is significantly different. This is a reflection of the model's relative insensitivity to the value of the relaxed modulus, particularly at lower temperatures where the modulus remains substantially higher than J_r throughout the course of the cure.

CONCLUSIONS

A model has been developed that allows the kinetic analysis of dynamic mechanical data and demonstrated on the TGDDM/DDS epoxy system.

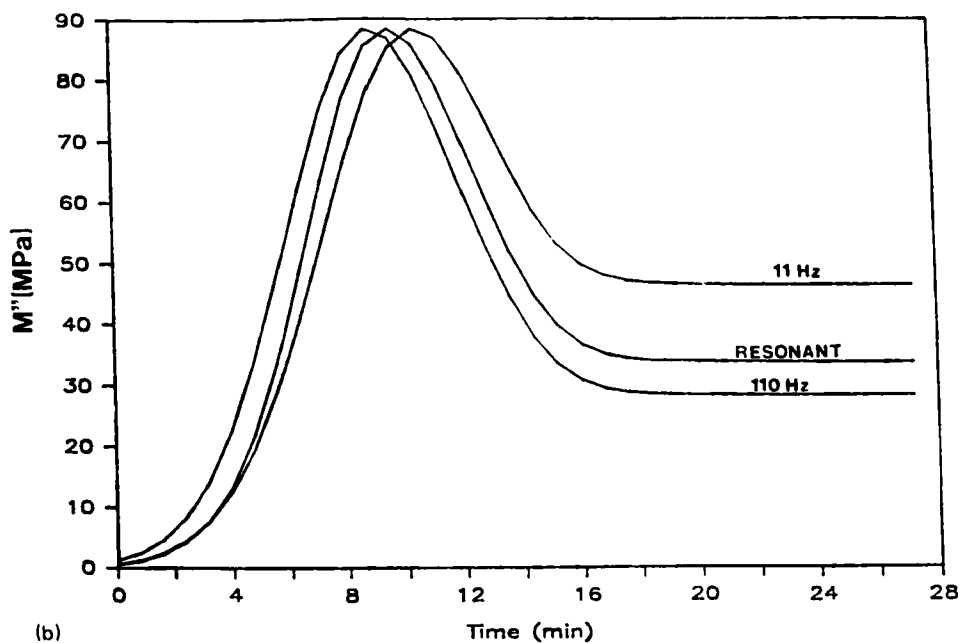
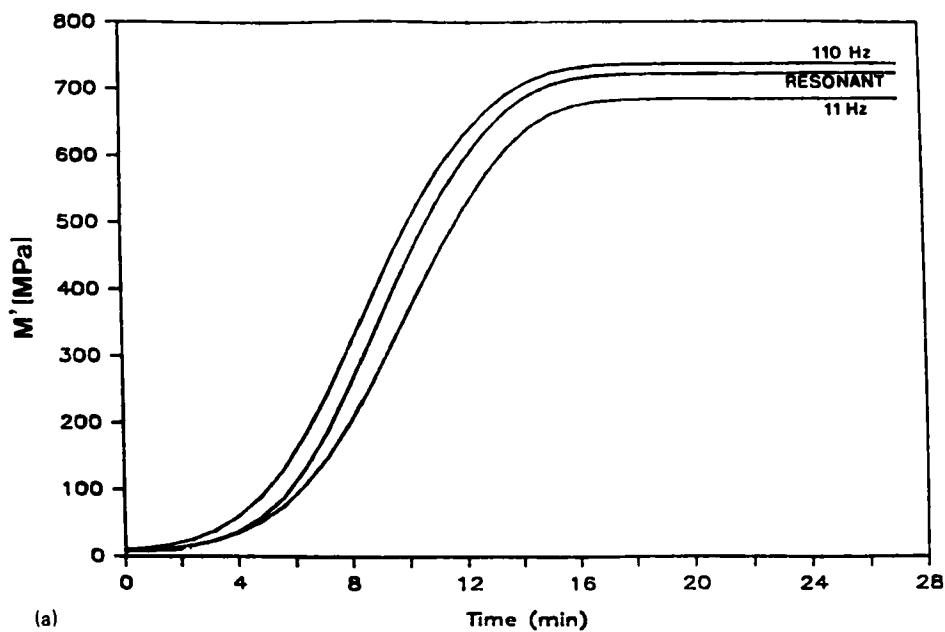


FIG. 4. Model predictions of effect of frequency on dynamic mechanical data of TGDDM/35 phr DDS plaque curing at 218°C. (a) Storage modulus. (b) Loss modulus.

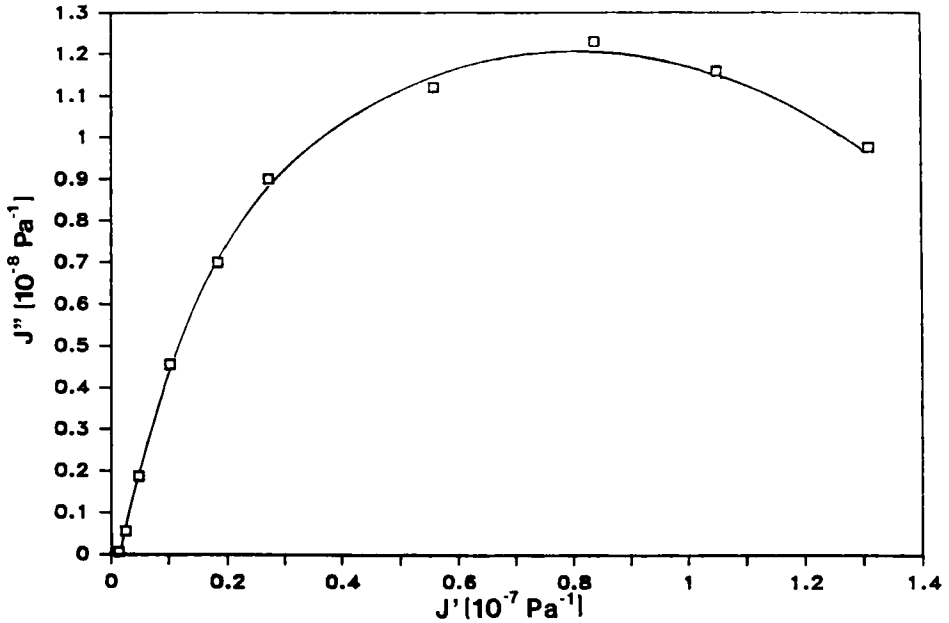


FIG. 5. Cole-Cole plot of loss compliance as a function of storage compliance for TGDDM/35 phr DDS cured at 218°C.

TABLE 4. Viscoelastic Parameters Obtained from Analysis of Cole-Cole Diagrams

Parameter	Temperature, °C			
	140	167	180	218
α	0.408	0.768	0.984	1.000
β	0.644	0.475	0.287	0.249
J_r, Pa^{-1}	5.11E-7	6.21E-6	5.00E-6	1.54E-7
J_u, Pa^{-1}	1.23E-9	1.37E-9	9.91E-10	1.21E-9

The model provides activation energies consistent with those obtained by other techniques of kinetic analysis.

This work has also demonstrated that the analogy between dielectric relaxation and viscoelastic relaxation of reacting systems may be exploited to develop a modeling methodology applicable to both. Furthermore, the use of Cole-Cole plots of loss compliance as a function of storage compliance for reacting systems can provide useful information.

The model presented here includes a viscoelastic component that allows the modeling of the complete dynamic mechanical behavior of a reacting system, rather than a single function. In addition, the viscoelastic model accounts explicitly for experimental frequency, thereby providing kinetic parameters which are independent of the frequency at which the data were taken. This allows the use of data taken at one frequency to be used to predict the behavior of the system at any other frequency.

The model presented here is a first step in the understanding of the effects of kinetic processes on the viscoelastic behavior of polymeric materials. Such understanding is necessary for the analysis of the mechanical properties of both neat polymers and composites whenever these properties are influenced by time-dependent changes in the system.

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