

Verification of the capability for quantitative stress prediction during epoxy cure

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We previously developed a formalism to calculate the evolution of stresses during the cure of crosslinking polymers. In the present study, we characterized the chemical kinetics and cure-dependent thermophysical properties for two epoxy systems, the diglycidyl ether of bisphenol A cured by either diethanolamine or a mixture of aromatic amines. Well-defined experiments were performed in which the cure stresses for these two epoxies were measured as a function of time. The stresses predicted by our formalism, using the material parameters obtained for the two systems, agreed well with the measured stresses. © 1997 Elsevier Science Ltd.

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INTRODUCTION

Overall goal

Calculations are now routinely performed to predict the stresses in polymers employed as electronic encapsulants, printed wiring boards, and composite structural members. These calculations can predict stresses in nonisothermal operation which arise from mismatch in the polymer and component coefficients of thermal expansion. For crosslinking polymers such as epoxies, however, stresses evolve during cure due to reaction exotherms, cure shrinkage, and imposed deformations. Only recently has a formalism for calculating stresses in such systems been developed¹. In this study, we have characterized the evolution of thermophysical properties in two model epoxies and have verified the accuracy of our formalism by predicting the evolution of stress in well-defined and well-monitored experiments. The calculated and measured stresses agreed well, allowing us to employ the formalism with confidence to problems of practical concern.

Theoretical formalism

The formalism has been documented extensively elsewhere¹ and will only be briefly sketched here. We assume that stresses accumulate only after the gel point. The state of stress, with both its deviatoric and bulk components, can be calculated as the reaction

proceeds by

$$\begin{aligned} \sigma = 2 \int_{-\infty}^t ds \left[G_d \left(\int_S \frac{du}{\tau(u)} \right) + \langle G_\infty(t, s) \rangle \right] \\ \left[\frac{d}{dt} \left(\gamma - \left\{ \frac{1}{3} \text{tr} \gamma \right\} I \right) \right] \\ + \int_{-\infty}^t ds K \left(\int_S \frac{du}{\tau(u)} \right) \left[\frac{d}{dt} (\text{tr} \gamma) I \right] \\ - \Psi (T - T_o) I - \Phi (p - p_{\text{gel}}) I \end{aligned} \quad (1)$$

where $G(t) = G_d(t) + G_\infty$ is the shear modulus, $K(t)$ is the bulk modulus, γ is the strain tensor, p and T are the extent of reaction and temperature, T_o is the temperature at the gel point p_{gel} , and I is the identity tensor. Ψ is a constant equal to the product of the glassy bulk modulus, K_g , and the glassy volumetric coefficient of thermal expansion, α_g (both independent of extent of reaction). Φ is also a constant equal to the product of the rubbery bulk modulus, K_∞ , and the total volumetric strain due to cure alone, ΔV_{rxn} (which is negative in sign). The four terms in equation (1) represent stresses arising respectively from imposed shear strains, imposed bulk strains, thermal expansion (or contraction) strains, and cure shrinkage strains.

The bulk modulus can be described phenomenologically by²

$$K(t) = \frac{K_g - K_\infty}{[1 + (t/\tau)]^{1/4}} + K_\infty \quad (2)$$

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and the decaying portion of the shear modulus for a wide range of epoxies at all post-gel extents of reaction has been shown to obey the theoretical relationships³

$$G_d(t) = \frac{G_g}{1 + (t/\tau)^{2/3}} \quad (3)$$

where G_g is the glassy shear modulus, which is independent of extent of reaction.

The characteristic relaxation time, τ , has the familiar WLF temperature dependence

$$\log \tau = \frac{-C_1(T - T_g)}{C_2 + T - T_g} \quad (4)$$

Equation (4) essentially defines the glassy transition as the temperature at which the characteristic relaxation time equals 1 s. The reference temperature, taken to be the glass transition temperature, itself depends on extent of reaction through the semi-empirical relationship⁴

$$T_g = \frac{T_g^o}{(1 - A_p)[1 - B(G_\infty/G_\infty^f)]} \quad (5)$$

where T_g^o is the T_g at the start of the reaction and G_∞^f is the rubbery equilibrium shear modulus at full cure. G_∞ is the equilibrium shear modulus at extent of reaction, p , which has been shown to obey our theoretical prediction of⁵

$$G_\infty(t) = G_\infty^f \left[\frac{p^2(t) - p_{gel}^2}{1 - p_{gel}^2} \right]^{8/3} \quad (6)$$

where p_{gel} is the extent of reaction at the gel point. A and B in equation (5) are constants describing the evolution of T_g with reaction and could be determined by evaluating T_g^f of the fully-cured polymer and of the critically-cured polymer, T_g^{gel} (i.e. cured to the gel point).

Prior to the gel point, the shear modulus is given by⁶

$$G_d(t) = \frac{G_g}{1 + (t/\tau)^{2/3}} e^{-(t/\lambda)^{2/5}} \quad (7)$$

where λ increases with extent of reaction according to the experimentally verified, theoretical prediction of

$$\lambda \sim \tau \left[\frac{p_{gel}^2 - p^2}{p_{gel}^2} \right]^4 \quad (8)$$

due to the increase in cluster size with reaction. Since the Newtonian viscosity is defined as

$$\eta_o = \int_0^\infty dt G(t) \quad (9)$$

the divergence of the relaxation time λ at the gel point leads to the divergence of the viscosity.

Finally, the 'average' equilibrium shear modulus, $\langle G_\infty(t, s) \rangle$, from equation (1) is usually equal to the equilibrium modulus, $G_\infty(t)$, of equation (6), which assumes that new crosslinks are inserted into the network in an unstrained state. If, however, viscoelastic relaxations are slow compared to the rate of reaction (an unusual circumstance), crosslinks may be inserted into the network in a strained state, and the 'average' equilibrium modulus is more complex (see ref. 7 for more details).

In our formalism, one calculates the extent of reaction

for arbitrary thermal history, uses the relationships above to relate thermophysical properties to extent of reaction, and calculates the stresses from equation (1). This procedure necessitates a knowledge of the reaction rate. A useful, yet phenomenological, rate law for epoxies is given by

$$\frac{dp}{dt} = (k_1 + k_2 p^m)(1 - p)^n \quad (10)$$

where k_1 and k_2 are reaction rate constants which are temperature dependent. Usually, k_i displays an Arrhenius temperature dependence, $k_1 = k_A = k_o \exp(-E/RT)$ where k_o is yet another constant and E is the activation energy. However, if the epoxy vitrifies during cure, such as in the 'B'-staging of printed wiring boards, the reaction will slow dramatically. A simple way to incorporate vitrification into the reaction rate law postulates that the characteristic reaction time constant, $1/k$, is the sum of two independent processes, one arising from the intrinsic Arrhenius rate and the second arising from viscoelastic mobility⁸. Therefore, the reaction rate constant k is given by

$$\frac{1}{k_i} = \frac{1}{k_A} + \omega\tau \quad (11)$$

where τ is viscoelastic time constant of equation (4) and ω is a constant which determines the severity of the reaction quench due to vitrification.

With all these equations, it might seem terribly tedious to determine all the parameters required for implementation. However, the list is relatively short, and the parameters are easily obtained. For example, one must fully-characterize the completely cured epoxy by obtaining the glassy and equilibrium shear and bulk moduli, G_g , G_∞ , K_g , K_∞ ; the WLF constants, C_1 and C_2 ; the glassy coefficient of thermal expansion, α_g ; and the glass transition temperature, T_g^f . The cure dependence of the glass transition can be fairly easily determined by further measurement of T_g for the initial and critical sample, T_g^o and T_g^{gel} . The reaction rate (i.e. dp/dt) must be determined, likely the most difficult task, but is typically already measured for processability studies. Finally, the extent of reaction at the gel point, p_{gel} , and the total volume change due to cure, ΔV_{rxn} , are required. If cure is nonisothermal, the thermal conductivity and heat capacity of the fully-cured sample and the heat of reaction are also needed. Most of these parameters are either normally determined (e.g. characterization of the fully-cured epoxy and reaction kinetics), easily determined (T_g^o , T_g^{gel} , p_{gel}), or accurately estimated (ΔV_{rxn} and thermal properties).

Model epoxies

Two epoxy systems were chosen as model systems. The epoxy resin in both cases was the diglycidyl ether of bisphenol A (Shell Epon 828, MW = 380). The curing agents, however, were radically different in their chemistry and reaction rate. The accuracy of the stress calculations should be indifferent to the chemistry details, so these distinct curatives offered a reasonable challenge to the universality of the formalism.

The curing agent in the first model system was diethanolamine (DEA). The secondary amine, being much more reactive than the neighbouring alcohol, quickly reacts to endcap the epoxy resin (roughly 10 min at the temperatures seen in this study, 65–90°C), while

the gel point occurs much later (at least 3 h). With the reactant ratios used here (89.3 wt% 828, 10.7 wt% DEA), we can consider the 'renormalized reactants' to be roughly half epoxy resin and half DEA-encapped resin. Therefore, the actual crosslinking proceeds not by the NH-epoxy reaction (since all secondary amines are pre-reacted), but by the tertiary-amine-catalysed epoxy-alcohol condensation. The precise crosslinking reaction mechanism is quite complex and changes from primarily this epoxy-alcohol condensation at temperatures below 70°C to progressively more tertiary-amine-catalysed epoxy homo-polymerization at higher temperatures (>90°C).

The curing agent in the second model system was a mixture of aromatic amines (Shell Curing Agent Z). Z is roughly 30 wt% metaphenylene diamine (MPDA), 20 wt% methylene diamine (MDA), 20 wt% of the adduct of phenyl glycidyl ether (PGE) and MDA, and 30 wt% of the PGE/MPDA adduct. The stoichiometric ratio was 83.3 wt% 828 epoxy resin to 16.7 wt% curing agent Z. In contrast to the complexity of the DEA system, Z curing agent offers almost textbook aromatic amine cure.

CHEMICAL KINETICS

Diethanolamine cure

The phenomenological cure kinetics for the 828/DEA system were determined by differential scanning calorimetry (d.s.c., Perkin Elmer System 7) and by Fourier transform infrared spectroscopy (FTi.r., Perkin Elmer System 2000). Both kinetic studies focused on the crosslinking reaction, so we defined time zero to occur immediately after the initial amine-epoxy adduct formation. In FTi.r. measurements, the epoxy concentration was obtained by monitoring the epoxy absorption at 916 cm^{-1} , which is distinct and can be integrated accurately. In d.s.c. measurements, the rate of heat generation was monitored and, as shown later, the normalized integrated d.s.c. signal closely tracked the extent of epoxy reaction measured by FTi.r. Therefore, we concluded that the major reaction exotherm is associated with the disappearance of the epoxide, and we feel confident that, even though the actual reaction mechanism is complex, we have a well-defined phenomenological measure of the crosslinking reaction.

The isothermal reaction rates obtained from d.s.c. at 70 and 90°C are shown in Figure 1. At 70°C, the reaction is clearly autocatalytic with a peak reaction rate at

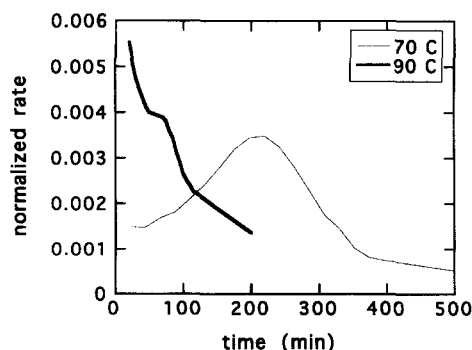


Figure 1 Isothermal reaction rates of 828/DEA at 70 and 90°C as measured by d.s.c. Note the change in reaction mechanism over this temperature range

roughly 200 min, but more closely resembles n th order kinetics at 90°C. If the reaction mechanism was constant with a typical activation energy, the reaction peak should appear at roughly 50 min at 90°C, and the data do exhibit a slight 'bump' near 65 min. Nevertheless, the distinct change in the shape of the reaction rate implies that the reaction mechanism, as stated previously, is changing as temperature increases. We can phenomenologically model the observed reaction rate as

$$\frac{dp}{dt} = (k_1 + k_2 p^m)(1-p)^{1.6} \quad (12)$$

for $T < 95^\circ\text{C}$

$$k_1 = (2.6 \times 10^7 \text{ min}^{-1}) \exp(-8000\text{K}/T)$$

for $T < 65^\circ\text{C}$

$$m = 2.2, \quad k_2 = (5.7 \times 10^8 \text{ min}^{-1}) \exp(-8000\text{K}/T)$$

for $65 < T < 90^\circ\text{C}$

$$k_2 = (9 \times 10^7 \text{ min}^{-1}) \frac{(90 - T)}{T^6} \quad [T \text{ in } ^\circ\text{C}]$$

$$m = 74 k_2 \quad [k_2 \text{ in } \text{min}^{-1}]$$

for $T > 90^\circ\text{C}$

$$m = k_2 = 0$$

where the odd temperature dependences of the reaction rate constant k_2 and exponent m display our disregard of the precise chemical details. In Figure 2, we compare the extents of reaction obtained from integrating the d.s.c. signal, from FTi.r. measurements, and from the predictions of equation (12) at 70 and 90°C. Considering the difficulties in determining conversions near the end of a reaction and the complex nature of DEA chemistry, the agreement is reasonable.

Aromatic amine cure

The cure kinetics of the Z-cured epoxy were much more rapid than the DEA-cured system but much more easily interpreted. The reaction rate was monitored by d.s.c. at temperatures from 80 to 110°C and was fit by

$$\frac{dp}{dt} = k_A(0.11 + p^{1.2})(1-p)^{1.35} \quad (13)$$

with $k_A = k_o \exp(-E/RT)$

where $k_o = 1.2 \times 10^6 \text{ min}^{-1}$ and $E = 12 \text{ kcal mol}^{-1}$ for all temperatures. The measured reaction rate, integrated extent of reaction, and theoretical extent of reaction

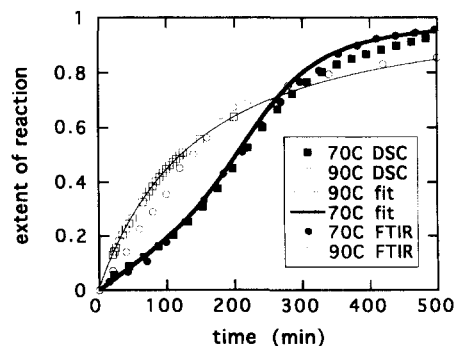


Figure 2 Comparisons of extents of reaction obtained from integration of the d.s.c. signal and from FTi.r. measurements

from equation (13) are shown in Figure 3 for an isothermal cure at 95°C.

THERMOPHYSICAL PROPERTIES DURING CURE

Glass transition and gel point

The increase in glass transition temperature with extent of reaction can be monitored in several ways. The following approach is fairly straightforward: mix the reactants and fill several d.s.c. sample pans, react isothermally for various times, remove from the oven and cool, and scan with the d.s.c. for the T_g . 828/DEA was reacted isothermally at either 65 or 90°C, while 828/Z was reacted at 95°C with a short post-bake at 180°C to complete the reaction. The time dependence of the increase in T_g is shown in Figure 4⁹. The dependence of T_g on extent of reaction could be described by equation (5) for both systems with

$$T_g(K) = \frac{260}{\left(1 - \frac{p}{5}\right) \left(1 - \frac{G_\infty}{15G_\infty^f}\right)} \quad \text{828/DEA} \quad (14)$$

$$T_g(K) = \frac{260}{\left(1 - \frac{p}{4}\right) \left(1 - \frac{G_\infty}{4G_\infty^f}\right)} \quad \text{828/Z} \quad (15)$$

and is shown in Figure 5.

We determined the gel time for DEA-cured epoxy by three independent techniques¹⁰. In the first, we measured the apparent viscosity at constant shear rate as a function of time, since the gel point is defined by the divergence of

the Newtonian viscosity. Alternatively, the gel point was determined by the time at which the loss and storage moduli exhibited the same power-law dependence on frequency, $G' \sim G'' \sim \omega^\Delta$. Finally, we cured the epoxy in an open tube in an oil bath and periodically 'poked' the sample. The gel point, defined as the first glimmer of solid-like behaviour, is obvious in this simple test. All three techniques yielded identical gel times, within experimental error. By converting the gel time to extent of reaction, we determined that the gel point for 828/DEA occurred at an extent of reaction of 0.65 for isothermal cures ranging from 65 to 90°C. For the 828/Z epoxy, we performed only the simple 'poke' test and found p_{gel} to be 0.75 for isothermal cures ranging from 50 to 95°C.

Thermal expansion and cure shrinkage

The linear coefficient of thermal expansion, $\beta = \alpha/3$, for the two model systems were measured previously with a Perkin Elmer System 7 Thermomechanical Analyser from -50 to 120°C. The data are presented in Figure 6 and the experimental procedure is detailed in ref. 11. For 828/DEA cured at 73°C for 16 h, the room temperature volumetric coefficient thermal expansion, α_g , equals $185 \times 10^{-6} \text{C}^{-1}$, and the rubbery value, α_r , equals $550 \times 10^{-6} \text{C}^{-1}$, which is three times larger than the glassy value. For 828/Z cured at 93°C for 16 h, α_g is $160 \times 10^{-6} \text{C}^{-1}$. Since this production cure schedule does not fully cure 828/Z, the rubbery value, α_r , was not measured. However, α_r/α_g is fairly constant even for dissimilar polymers¹², and since 828/Z and 828/DEA are both roughly 85 wt% 828 resin, we assumed $\alpha_r = 3\alpha_g$ here as well.

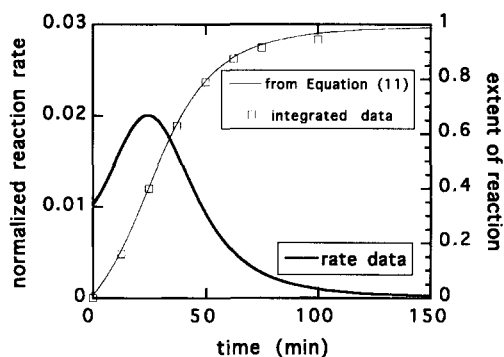


Figure 3 Isothermal reaction rate and extent of reaction from d.s.c. and theoretical extent of reaction for 828/Z at 95°C

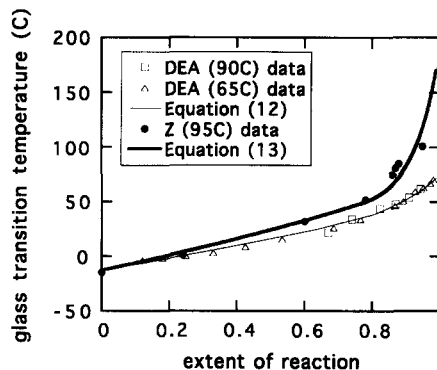


Figure 5 Comparison of measured and theoretical dependence of the glass transition temperature on extent of reaction for 828/DEA cured at 65 and 90°C

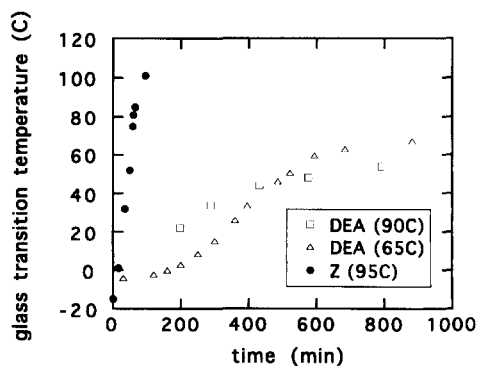


Figure 4 Increase in glass transition temperature with time as the 828/DEA reaction progresses isothermally at 65 and 90°C

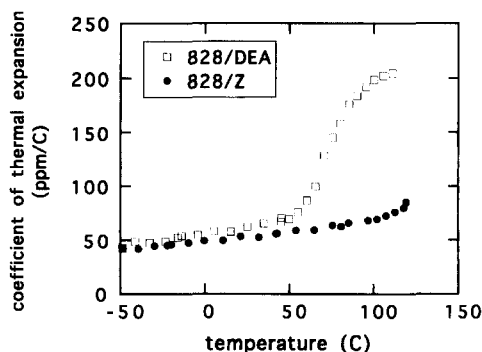


Figure 6 The temperature dependence of the linear coefficient of thermal expansion for 828/DEA and 828/Z measured by t.m.a.

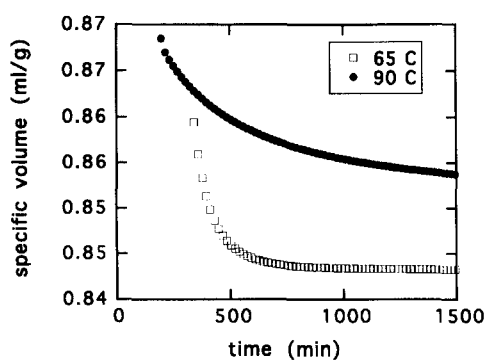


Figure 7 Volume change with time during the cure of 828/DEA at 65 and 90°C

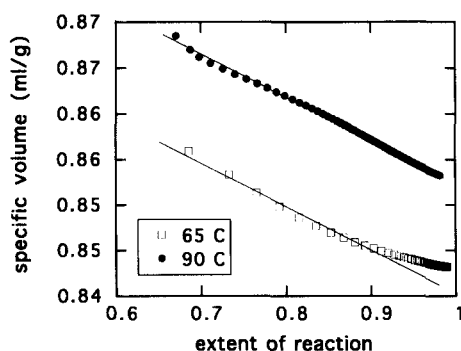


Figure 8 Volume change as a function of extent of reaction during the cure of 828/DEA at 65 and 90°C

The volume change upon cure for 828/DEA was also measured previously with a custom mercury dilatometer¹³. The samples were cured isothermally at 65 and 90°C to their respective gel points, cooled, transferred to the dilatometer, heated again to the cure temperature, and fully cured while monitoring the volume. The results are shown in Figure 7 as a function of time and in Figure 8 as a function of extent of reaction.

We assumed in equation (1) that the volume shrinkage is proportional to the extent of reaction, which is verified by the 90°C data. We have also assumed, for reasons detailed in ref. 14, that the product, Φ , of the bulk modulus and the incremental cure volume change is constant. In contrast to the 90°C cure, vitrification will occur during the 65°C cure since the T_g of the fully-cured 828/DEA system is 75°C. In addition, since the glassy bulk modulus is larger than the rubbery bulk modulus, our assumption of constant Φ implies that, for the 65°C cure, the rate of volume shrinkage with extent of reaction should begin to slow as the T_g approaches the cure temperature. The data in Figure 8 support this hypothesis. The measured volumetric strain due to the cure of 828/DEA after the gel point is 1.9%. Assuming that the cure strain is always proportional to the extent of reaction, this would extrapolate to a total cure shrinkage of 5.5%.

The rapid cure of 828/Z precludes direct measurement of the cure shrinkage by the method employed for 828/DEA. The successful correlation of 828/DEA shrinkage with extent of reaction emboldens us to propose the same behaviour for 828/Z. Moreover, since the two systems are chemically similar (both roughly 85 wt% 828 resin), we will assume that 828/Z also experiences 5.5% total cure shrinkage. Since the extent of reaction at the gel

point of this system was determined above to be 0.75, the total cure shrinkage past the gel point is 1.4%. While not rigorous, we expect this procedure to be reasonably accurate. Moreover, not much else can be done!

Shear and bulk modulus

The room temperature bulk and shear moduli for both the DEA and Z cured systems were measured previously and the procedure was described in detail¹⁵. Briefly, for measuring the bulk modulus, the samples were strain gauged, immersed in a silicone fluid, and pressurized to 1000 psi. The shear moduli were measured with a Rheometrics RDS-2 using rectangular torsion geometry ($0.125 \times 0.5 \times 2''$). The linear elastic bulk moduli were 5.1 and 5.3×10^9 Pa for the fully-cured 828/DEA and 828/Z epoxies at 22°C, while the shear moduli were 1.0 and 1.2×10^9 Pa respectively. These moduli yield Poisson's ratios for the DEA and Z-cured epoxies of 0.41 and 0.40, which is in agreement with literature epoxy values.

The WLF parameters were also determined in this previous study¹⁵ for the 828/DEA epoxy from linear viscoelastic oscillatory shear moduli at temperatures from 70 to 90°C obtained using the Rheometrics. For a nominally fully-cured sample (T_g of 70°C), the WLF parameters were $C_1 = 14.2$ and $C_2 = 40.4$ for a reference temperature of T_g . The shift factors for a nominally fully-cured 828/Z epoxy (T_g of 185°C) were determined over temperatures from 190 to 210°C in ref. 3, where we found $C_1 = 12.4$ and $C_2 = 43.8$ for a reference temperature of T_g .

We previously developed a theory¹⁶ which proposed the cure-independent shear relaxation spectrum of equation (3) and the cure-dependence of the equilibrium modulus of equation (6). As seen in Figure 9, the fully-cured epoxies both exhibited the predicted relaxation spectrum³. The ultimate equilibrium moduli for 828/DEA and 828/Z were 7×10^6 and 1.4×10^7 Pa, respectively. In Figures 10¹³ and 11⁵, the increase in equilibrium modulus with extent of reaction at 65 and 90°C for 828/DEA was measured and found to agree well with equation (6).

Viscosity

Prior to the gel point, we measured the divergence of the Newtonian viscosity for the 828/DEA systems¹⁰ using the Rheometrics RDS-2 with either parallel plate or Couette geometries. The slow reaction kinetics allowed ample time for measurements at 90°C. Near

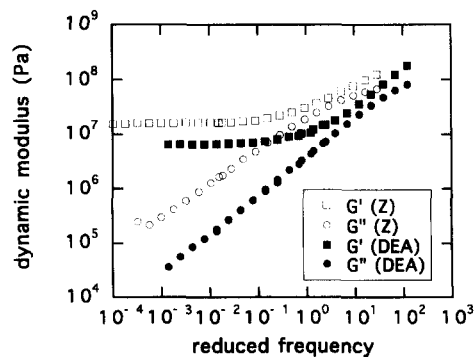


Figure 9 Master curves for the dynamic shear moduli of 828/DEA and 828/Z at reference temperatures of their respective T_g . Note that the spectrum of relaxation times for both systems is described well by a power law with exponent equal to $-2/3$

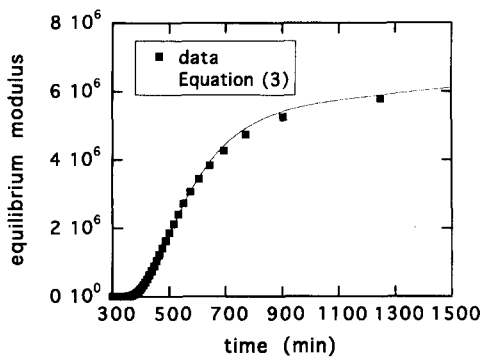


Figure 10 The measured and predicted increase in equilibrium modulus with time as 828/DEA isothermally cures at 65°C

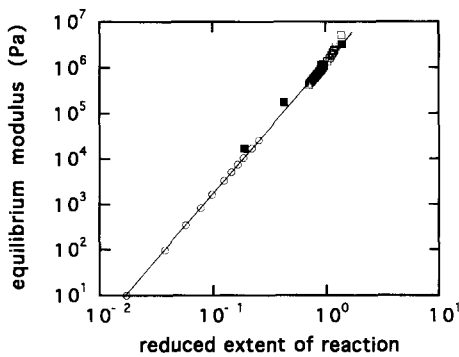


Figure 11 The increase in equilibrium modulus with extent of reaction for 828/DEA isothermally cured at 90°C. The measured slope of 2.8 ± 0.2 agrees well with the theoretical prediction of $8/3$

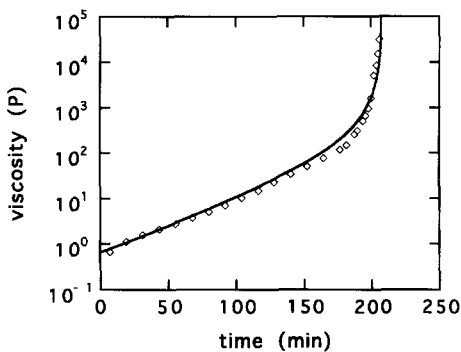


Figure 12 The measured and predicted divergence of the Newtonian viscosity during the cure of 828/DEA

the gel point, care was taken to ensure that the apparent viscosity was actually Newtonian (by measuring the divergence at various shear rates in separate experiments). Figure 12 shows the measured divergence and the Newtonian viscosity predicted by equations (7)–(9) which agree well. The initial slow increase in viscosity is due to both the increase in average cluster size and the increase in glass transition temperature, while the steep increase near the gel point is due primarily to the topological divergence.

Thermal properties

For nonisothermal operation, we also require the thermal conductivity, the heat capacity, and the heat of reaction. The measured heats of reaction, obtained from the integrated d.s.c. traces used in generating the reaction rates of equations (12) and (13), were 200 and 400 J g⁻¹

respectively for the DEA and Z-cured epoxies. The thermal conductivities were reported in the literature¹⁷ as 0.16 and 0.17 W (m-K)⁻¹ for 828/DEA and 828/Z, and should be fairly insensitive to the glassy transition¹². The rubbery and glassy heat capacities for the DEA-cured epoxy were found by d.s.c. to be relatively independent of extent of reaction and equal to 1.4 and 2.1 J (g-K)⁻¹ in the glassy and rubbery state respectively.

EXPERIMENTAL VERIFICATION OF THE FORMALISM

Cures entirely above T_g with imposed shear strains

To verify the formalism and the accuracy of our material characterization, we need to deform the curing epoxy in various geometries and under different thermal profiles. In these first tests, we concentrate on the increase in equilibrium shear modulus with extent of reaction. Therefore, we are, by design, always at temperatures above the T_g. In this specific study, we imposed a shear strain, measured the shear stress, and compared it to our theoretical predictions. The shear strain was a simple sinusoid, but in contrast to typical sinusoidal measurements at high frequencies (~1 Hz) and low strains (which yields the linear viscoelastic storage and loss moduli, G' and G''), the applied strain had a large amplitude and a long period over which considerable reaction occurred.

In Figure 13, we show the stress measured on the Rheometrics RDS-2 with cone-and-plate geometry for 828/DEA cured isothermally at 90°C. The imposed strain had an amplitude of 5% and a frequency of π/1800 rad s⁻¹. From equation (12), the gel time at 90°C is calculated to be 12 450 s, and the onset of a measurable stress does agree with this prediction. At the completion of the test at 25 000 s (~7 h), the reaction is predicted to be 82% complete. The agreement between theory and experiment in Figure 13 is quite satisfying.

In Figure 14, we show similar results for 828/Z cured isothermally at 95°C for a strain of 5% amplitude and π/450 rad s⁻¹ frequency. From equation (13), the gel time at 95°C is calculated to be 2750 s, and the onset of a measurable stress occurs roughly 90 s earlier. At the completion of the test at 1 h, the reaction is predicted to be 87% complete. Again, the agreement between theory and experiment is reassuring.

It may not be obvious that this sinusoidal strain test is quite sensitive to the parameters used in the formalism.

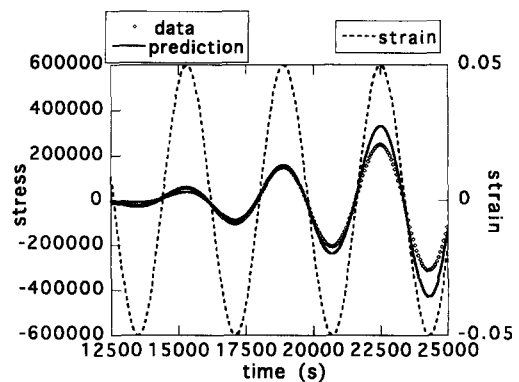


Figure 13 The stress in response to a slow sinusoidal strain as 828/DEA cures at 90°C as measured experimentally and predicted by theory. The gel time is 12 450 s

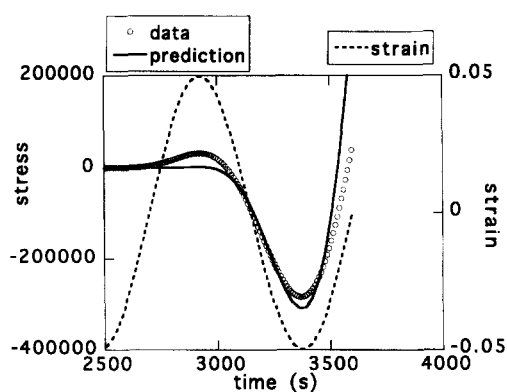


Figure 14 The stress in response to a slow sinusoidal strain as 828/Z cures at 95°C as measured experimentally and predicted by theory. The gel time is 2750 s

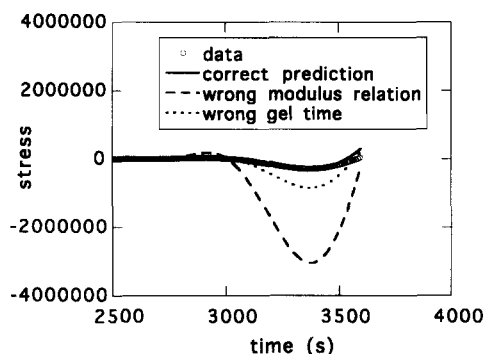


Figure 15 Small errors in characterizing the chemical kinetics or the dependence of the modulus upon cure can lead to large errors in the predicted stress for this type of experiment

For example, how would the predictions change if the gel time were 3 min earlier than observed? Or, how would they change if the equilibrium modulus did not increase with extent of reaction as in equation (6) with an exponent of $8/3$, but with the mean-field exponent of one? These predictions are compared to the correct predictions and the measured stress in Figure 15. As clearly seen, these rather small changes in material characterization result in dramatically poorer predictive accuracy. Therefore, this type of test does severely challenge our formalism and our characterization of the epoxies, and we feel confident in our ability to capture accurately the stresses generated as the equilibrium shear modulus increases with cure for arbitrary strain histories.

Cures with vitrification

Before diving into calculation of stresses during cures with vitrification, it is important to define exactly what we mean by the glass transition temperature. We will simply assume that the glass transition is a purely dynamic phenomenon, which arises from some external rate exceeding a corresponding internal relaxation rate, which effectively quenches the system dynamics. A reasonable and unambiguous definition of T_g within this framework can be succinctly posed; the glass transition temperature is the temperature at which the shortest characteristic relaxation time, τ , of equations (2) and (3) equals 1 s. This definition captures the practical fact that most experiments chosen to probe the glassy transition operate in the 1 Hz regime.

We first determined the consistency of T_g from various experiments. Samples of 828/DEA were fully-cured at 90°C and were subjected to the following tests. The change in heat capacity was determined by d.s.c. (Perkin-Elmer DSC-7) at a ramp rate of 1°C min^{-1} . The change in coefficient of thermal expansion was determined by monitoring the volume by thermomechanical analysis (Perkin-Elmer TMA-7) at a ramp rate of 1°C min^{-1} . The temperature dependent shear modulus was measured with the Rheometrics RDS2 at 1 Hz in torsion rectangular geometry at a ramp rate of 1°C min^{-1} . Finally, we followed the change in length of a rectangular sample heated at a ramp rate of 1°C min^{-1} to which a dead weight was attached. Since these results should apply to partially cured as well as completely cured epoxies, we purposefully did not anneal any of the samples for the above tests. Therefore, the results do exhibit the peculiar 'bumps' associated with unequal heating and cooling rates.

Figures 16 and 17 portray the results of these experiments by consistent definition of the transition onset, we observe differences of only a couple degrees between the various techniques. Two conclusions can be made at this juncture; any convenient technique is appropriate for determination of the glassy transition, and the shear and bulk characteristic times, τ , defined in equations (2) and (3) are identical.

We can now proceed to tests on curing epoxies which vitrify during the cure cycle. In this test, we concentrate

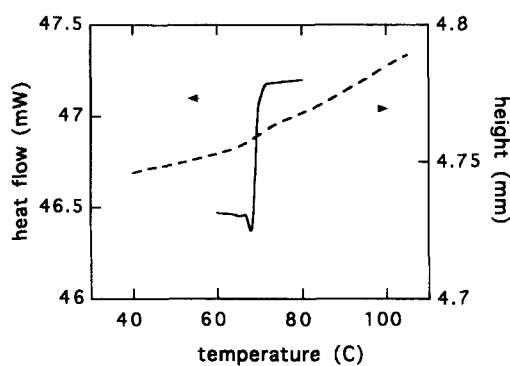


Figure 16 T_g 's as measured by d.s.c. (heat flow) and t.m.a. (height) for 828/DEA. Both techniques yield similar onset values: 64°C for d.s.c. and 66°C for t.m.a.

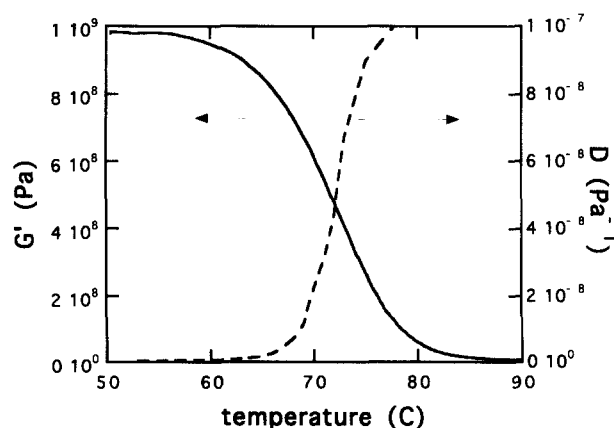


Figure 17 T_g 's as measured by oscillatory shear rheometry (G') and tensile creep (D) for 828/DEA. Both techniques yield similar onset values: 65°C in shear and 68°C in tension

on our ability to accurately predict the increase in glass transition with extent of reaction for complicated thermal cure profiles. We first cured 828/DEA isothermally at 35°C for three days. During this first stage, the T_g exceeded the cure temperature and the epoxy vitrified. From the value of T_g at this point, 54°C, and our knowledge of the chemical kinetics in equation (12), we found that ω , required in equation (11), must be 10^{-8} . As a slight digression, 828/Z cured for one day at 93°C, yields a T_g of 115°C which is also accurately predicted by a value of 10^{-8} for ω .

After this initial cure at 35°C, the sample was cooled to 25°C in a DMA (Perkin-Elmer System 7), heated at $0.2^\circ\text{C min}^{-1}$ to 75°C, cooled at 2°C min^{-1} to 25°C, reheated at $0.2^\circ\text{C min}^{-1}$ to 75°C, cooled at 2°C min^{-1} to 25°C, heated at $0.2^\circ\text{C min}^{-1}$ to 75°C, held for 300 min at 75°C, and finally cooled at 2°C min^{-1} to 25°C. During this complicated thermal schedule, we measured the dynamic moduli with a penetration probe oscillating at 1 Hz with a 1200 mN applied dynamic force. The indentation modulus measured in such an experiment is most closely related to the dynamic Young's modulus. Since we demonstrated above that all experimental procedures yielded similar values for T_g onset, we calculated Young's moduli with our formalism and compared the predicted T_g s (Young's) to those measured (indentation). The measured and predicted moduli, normalized by their respectively glassy values, are shown in Figure 18. The measured and predicted onset T_g s are shown in Figure 19. Given the complicated thermal profile which cycled through T_g and the inherent imprecision in defining the onset of the glassy transition,

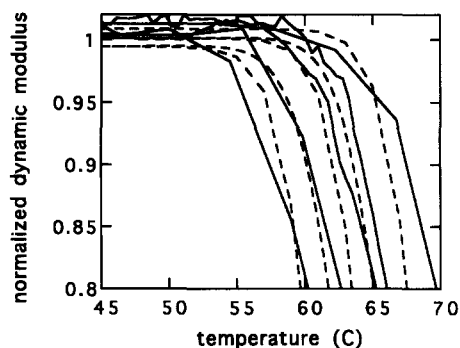


Figure 18 The normalized dynamic penetration moduli measured by t.m.a. (solid lines) and the normalized predicted dynamic tensile moduli (dashed lines) as 828/DEA cures during successive cooling and heating ramps

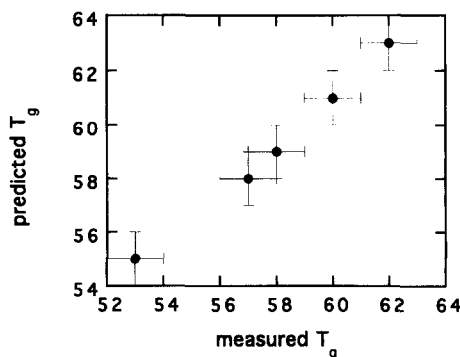


Figure 19 Measured and predicted values for the onset of T_g obtained from Figure 18

the level of agreement between theory and experiment is once again reasonable. Therefore, we feel confident that our formalism and material characterization can accurately capture the increase in T_g with cure for arbitrary thermal histories.

Cures with bulk strains

In our final tests, we focus on our ability to capture stresses during cure with bulk strains, in particular, cure shrinkage strains. The experimental apparatus consisted of two thin-walled aluminium tubes filled with 828/DEA which were cured nominally isothermally¹³. One tube was instrumented with strain gauges to measure the hoop and axial strains at three points around the circumference of the middle of the tube. The second tube was fitted with thermocouples to measure the surface temperature histories of the outer and inner tube walls and in the epoxy near the tube centre (see Figure 20). Three experiments were performed differing only in the nominal oven temperature, 65, 73, or 90°C. Since the T_g of 828/DEA at the end of these tests will be roughly 70°C, the three cure temperatures represent cases of increasingly less important viscoelasticity. From a model validation perspective, this geometry accentuates the contribution of the bulk modulus, K , to the cure stress since the 'applied' strain equals the cure shrinkage and represents another unique test of the formalism.

To calculate the cure stresses in this experiment, we needed to employ finite element codes. The details of the development of these codes will be discussed elsewhere, but in general they proceeded as follows. The thermal and extent of reaction time histories for each element were calculated separately first, since this problem could be decoupled from the stress calculations. We did not attempt to model convection in the oven, but, rather, set the outer wall temperature history of the aluminium tube equal to the measured history. The output from these thermal calculations was then fed to the stress codes which incorporated the formalism presented above. An iterative solution technique was employed, and unique routines were developed to solve this problem where such a large difference between the magnitudes of the deviatoric and bulk moduli existed.

The predicted and measured centreline temperature histories are shown in Figures 21-23 for the three oven cures. The agreement is quite good with the greatest discrepancy occurring at early times where our knowledge of the exact epoxy temperature is somewhat uncertain since the epoxy has just been mixed, poured into the tubes, and placed into the oven. The corresponding plots comparing measured and predicted hoop

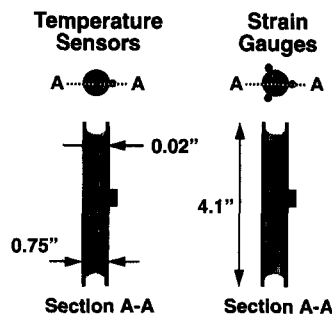


Figure 20 Sketch of the thin walled tubes showing the positions of thermocouples and strain gauges

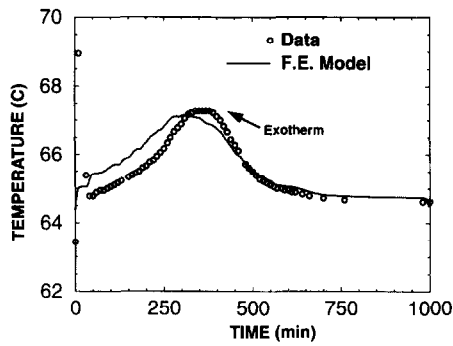


Figure 21 Measured and predicted temperature profiles as 828/DEA cures in thin walled tubes at an oven temperature of 65°C

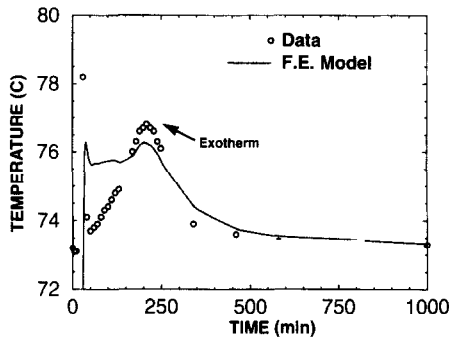


Figure 22 Measured and predicted temperature profiles as 828/DEA cures in thin walled tubes at an oven temperature of 73°C

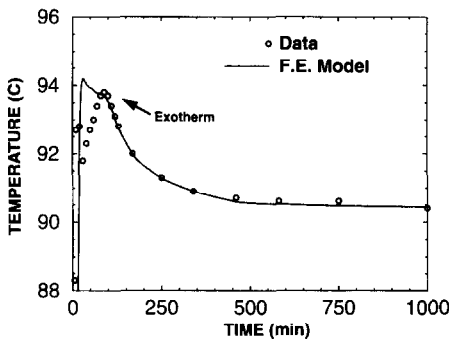


Figure 23 Measured and predicted temperature profiles as 828/DEA cures in thin walled tubes at an oven temperature of 90°C

strains are given in Figures 24–26. Predictions and measurements agree extremely well for the 65 and 73°C cures where the epoxy vitrifies near reaction completion. For the 90°C cure, data and experiment agree up to 500 min, at which time the epoxy is 85% reacted. After this point, however, the averaged measured hoop strain exceeds the predicted value. In fact, the actual stresses became so large at 900 min that the sample broke. Nevertheless, from our success at 65 and 73°C and at 90°C up to 85% reaction, we are pleased with our ability to model quantitatively bulk stresses that arise from cure shrinkage.

CONCLUSIONS

The formalism presented in this paper truly represents a unique description of stress generation during cure. By thorough material characterization and model validation, we now feel that we can use the formalism with confidence in practical problems. We are currently

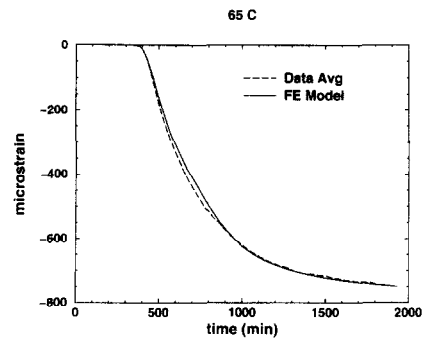


Figure 24 Measured and predicted hoop strains as 828/DEA cures in thin walled tubes at an oven temperature of 65°C

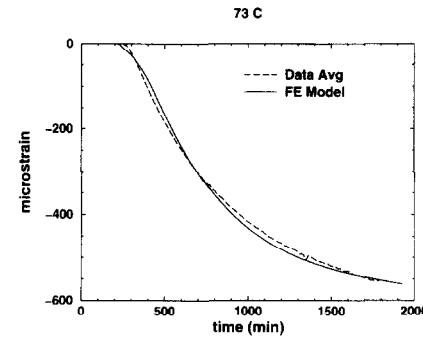


Figure 25 Measured and predicted hoop strains as 828/DEA cures in thin walled tubes at an oven temperature of 73°C

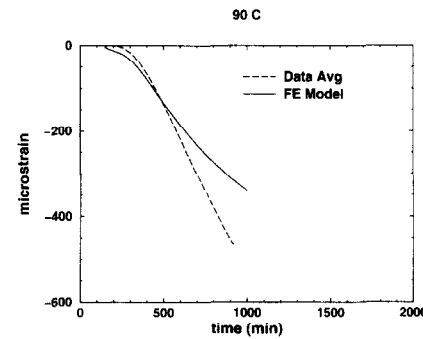


Figure 26 Measured and predicted hoop strains as 828/DEA cures in thin walled tubes at an oven temperature of 90°C

attempting to optimize the cure schedule for an epoxy encapsulated computer chip and neutron generator at SNL for which we believe operation difficulties have arisen due to cure-induced stresses. We envision that this approach can also be applied to industrial problems (e.g. aerospace, automotive) where residual stresses (potential failure) or strains (dimensional instability) are of concern.

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