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Constitutive Equation for Cure-Induced Stresses in a Viscoelastic Material[†]

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ABSTRACT: Branched polymer systems such as epoxies, polyurethanes, etc., can develop significant stresses during cure. These stresses principally arise from the shrinkage caused by chemical reactions in the postgel regime and can result in cracking of the material. In this paper we drive a constitutive equation that describes the development of elastic and viscoelastic stresses during cure. An interesting coupling is found between the equilibrium and relaxing components of the stress, due to the memory effects present in a viscoelastic fluid. These memory effects increase the residual elastic stresses at infinite time.

Introduction

Cure shrinkage, and subsequent cracking of a material, is a ubiquitous problem, occurring in such diverse materials as ceramic green bodies, polymeric resins, paints, and wood. In some cases, such as the drying of wood and ceramics, the root cause of cracking is the compositional inhomogeneities that arise from evaporation of the liquid. In polymeric encapsulants such as epoxy resins, cure stresses arise from the volume change that accompanies cross-linking. Shrinkage stresses are negligible well before the gel point, due to flow of the liquid encapsulant; however, beyond the gel point the shear and tensile moduli become substantial and cure stresses can exceed the strength of the material, causing stress relief through cracking. For this reason, there have been a number of experimental studies of the development of cure stresses.[1–4]

Encapsulation is usually done in an open geometry, where the volume change that accompanies cure is readily accommodated by flow of the encapsulant, and the potentially large hydrostatic stresses that can arise from the bulk modulus are avoided. Since the bulk modulus is typically several orders of magnitude larger than the shear or tensile moduli, it is appropriate to think of the cure shrinkage as inducing strains on the system, which then create stress via the shear and tensile relaxation moduli. Many real applications involve complex geometries (e.g., electrical circuits), so stress calculations must be done with finite element codes. These calculations require detailed information about the properties of the encapsulant, including the change in volume with degree of cure, the cure kinetics, and the shear and tensile relaxation moduli as a function of cure. Finally, a constitutive equation is required, and the development of the appropriate equation is the main goal of this paper.

Stress calculations are straightforward for a fluid with time-independent viscoelastic properties. However, the viscoelastic properties of curing materials change rapidly with time, leading to questions about the form of the constitutive equation. In this paper we develop a constitutive equation for stress development in the postgelation stage, where stresses can be large. We find an interesting coupling between the equilibrium and relaxing components of the stress, the net result of which is to increase the equilibrium stresses in the material relative to those equilibrium stresses that would develop in an asymptotically slow cure.

To better understand the problem of stress development, it is helpful to give a preliminary description of the shear or tensile stresses that can arise in a curing system. When a normal viscoelastic fluid is subjected to an imposed time-dependent shear or tensile strain, $\gamma(t)$, a stress, $\sigma(t)$, will arise. This stress will have a relaxing component, $\sigma_r(t)$, that is due to the relaxing component of the modulus and an equilibrium component, $\sigma_\infty(t)$, that is due to the equilibrium modulus of the material. If the applied strain is stopped at time t, the relaxing component of the stress will gradually dissipate, until at infinite time only the equilibrium component will remain. If the material is unstrained at $t = 0$, then the equilibrium stress is just $\sigma_\infty(t) = \gamma(t)\, G_\infty$, where G_∞ is the equilibrium modulus. Likewise, the relaxing component of the stress can be computed from the relaxing component of the modulus, $G_r(t)$, by using the Boltzmann superposition relation,[5] $\sigma_r(t) = \int \mathrm{d}s\, G_r(t-s)\, \dot{\gamma}(s)$. In the simple case where an instantaneous strain γ is made at $t = 0$, the stress at time t is $\sigma_r(t) = \gamma G_r(t)$.

In a curing material, the physical properties change continuously with time, due to the chemical reactions that occur. In general, a chemical reaction has an associated volume change, and since the bulk modulus is generally large, force blances in the potted material create shear and tensile strains. As this volume relaxation occurs, the shear and tensile moduli change, since these depend indirectly on time, through the time-dependent extent of reaction, ϵ_t. Thus the equilibrium modulus, $G_\infty(\epsilon_t)$, and the relaxing modulus, $G_r(t, \epsilon_t)$, contain an explicit dependence on the extent of reaction. However, the cure-induced strain, $\gamma(t)$, still depends on time directly, since there may be considerable time lag between the extent of reaction and the volume relaxation, an effect that is very pronounced in the glassy state. Also, external forces can create time-dependent strains that have nothing to do with chemical reactions.

Although the concepts of equilibrium and relaxing stresses in time-dependent viscoelastic fluids are useful for analysis, it should be noted that experimentally separating these stresses in curing materials would be difficult. For example, to measure the equilibrium stress at time t, one would have to quench the chemical reaction and monitor the stress until the relaxing component had essentially vanished. Corrections would then have to be made for any strains that occurred after time t, such as might arise from slow volume relaxations. Having defined some basic concepts and terminology, we now proceed to the constitutive equation for stress development in the postgel state.

Theory

Memory Effects in Equilibrium Stresses. In order to illustrate the difficulties encountered with stress

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calculations in a material with a time-dependent equilibrium modulus, we consider the limiting cases of small and large viscoelastic memory throughout the duration of cure.

The development of cure stresses is straightforward for the slow cure of a material with short relaxation times. Memory effects are then negligible, and the incremental equilibrium stress (the increase in the *nondecaying* part of the stress) is due solely to strains that arise either from the shrinkage of the material or from external stresses. The incremental equilibrium stress is thus the product of the incremental strain times the current elastic modulus, $\delta\sigma_\infty(t) = G_\infty(\epsilon_t)\ \delta\gamma(t)$, which gives the zero-memory stress limit[1]

$$\sigma_\infty(t) = \int_0^t \mathrm{d}s\ G_\infty(\epsilon_s)\ \dot{\gamma}(s) \tag{1}$$

where $\dot{\gamma}$ is the time derivative of γ. This formula has been successfully employed to fit experimental cure shrinkage data taken in the slow cure limit.[1]

When the material has relaxation times that are long compared to the cure time, there will be substantial memory effects in the material. These will be manifested through a decaying, viscoelastic contribution to the stress and through an additional equilibrium elastic contribution to the stress, due to memory effects in the material. In the limit where the cure time is small compared to the viscoelastic relaxation times, the additional equilibrium elastic contribution is the incremental modulus times the overall strain, leading to the complete differential $\delta\sigma_\infty(t) = G_\infty(\epsilon_t)\cdot\delta\gamma(t) + \gamma(t)\ \delta G_\infty(\epsilon_t)$. Summing gives the maximum possible equilibrium elastic stress

$$\sigma_\infty(t) = \gamma(t)\ G_\infty(\epsilon_t) \tag{2}$$

Physically, this implies that cross-linking takes place in a system that is affinely deformed relative to its strain state at the gel point. This stress is much larger than the stress in eq 1, where the final modulus is replaced by a modulus averaged over the strain. In numerical terms, strong memory increases the equilibrium stress by a factor of ~2–4. Note that the derivation of eq 2 implies that the decaying component of the stress will dominate the equilibrium component throughout the cure cycle; only long after cure will the measured stress be due to eq 2.

Real polymeric materials have a decaying memory of previous states of strain, so the actual equilibrium stress lies between the limits in eqs 1 and 2. Moreover, the viscoelastic properties of branched polymers evolve with time, with dramatic memory effects occurring both at the sol–gel transition and near the glassy transition temperature. Since the glassy transition temperature often increases above the reaction temperature during the later stages of the cure cycle, this can be an important effect. In the following, we derive a constitutive equation for the evolution of equilibrium and relaxing stresses during the cure of a viscoelastic material. The result for the equilibrium stress smoothly interpolates between the weak and strong memory limits given above.

Time-Dependent Modulus for a Gelling Material. In order to develop a constitutive equation for a gelling system, it is necessary to have some idea of the structural and viscoelastic transformations during cure. Fortunately, there has been much recent progress in the study of the structural aspects of gelation, and it is now known that many systems are well described by percolation. Likewise, percolation-based theories have been proposed[6–9] that give a good description of the time-dependent linear viscoelasticity in epoxy systems.[10,11] In the following we give a brief description of the percolation theory and its relation to viscoelasticity.

In the bond percolation model,[12,13] monomers occupying sites on a 3-dimensional lattice are randomly bonded with probability ϵ. When ϵ is small, only a few dimers and trimers are formed, but as ϵ increases, very large branched polymers appear, until at a critical extent of reaction, ϵ_c, an infinite cluster appears and certain average cluster sizes diverge. Thus, $\epsilon = \epsilon_c$ markes the transition from the sol to the gel. Beyond ϵ_c the largest clusters become attached to the infinite cluster to form a network, within which are embedded finite clusters whose average size decreases as ϵ approaches 1. Near the sol–gel transition the percolation model is analogous to a continuous phase transition in that many quantities diverge as powers of $|\epsilon - \epsilon_c|$. For example, as the gel point is approached from below, the viscosity diverges[6] as $\eta \sim |\epsilon - \epsilon_c|^{-k}$ ($k \cong {}^4/_3$), and above the gel point the elastic shear or tensile modulus of the infinite network increases[6] as $G_\infty \sim |\epsilon - \epsilon_c|^z$ ($z \cong {}^8/_3$).

The relaxation times for a melt of branched polymers can be obtained by considering the translational, rotational, and configurational dynamics of a single cluster. An assumption of self-similar Brownian dynamics leads to the relaxation time spectrum[6]

$$H(\tau)\ \mathrm{d}\ln\tau = \frac{1}{\tau^{3/(2+D)}} f(\tau/\tau_z)\ \mathrm{d}\ln\tau \tag{3}$$

for a melt of branched polymers near the gel point. The exponent $D \cong 2.5$ is the fractal dimension of a typical cluster and so relates the cluster radius and mass by $R^D \sim m$. This expression is valid for times larger than the relaxation time of the fastest Rouse mode, τ_0. The function $f(x)$ is a rapidly decaying function that essentially truncates the relaxation time spectrum at τ_z.

The important aspect of eq 3 is the appearance of the *viscoelastic exponent* $3/(2 + D) \cong {}^2/_3$. By taking transforms, it can be shown[6] that the tensile or shear relaxation modulus has the very slow, power law decay $G(t) \sim t^{-2/3}$ for $\tau_0 < t < \tau_z$, and the complex modulus has the form $|G^*| \sim \omega^{2/3}$ for $1/\tau_0 > \omega > 1/\tau_z$. A power law decay is sufficiently slow that a resin retains significant stress even at large times after deformation. Finally, beyond the gel point the relaxation time τ_z *decreases* as $|\epsilon - \epsilon_c|^{-4}$ as the largest clusters, with the longest relaxation times, attach to the infinite network.[6,7] Thus the slowest decays occur in the vicinity of the gel point.

In summary, the time-dependent modulus in the postgelation regime can be written

$$G(t,\epsilon_t) = G_r(t,\epsilon_t) + G_\infty(\epsilon_t) \tag{4}$$

where G_∞ is the equilibrium modulus and G_r is the relaxational part of the modulus. The equilibrium modulus is zero before the gel point ϵ_c but just beyond the gel point grows as the power law $G_\infty = G \times (\epsilon - \epsilon_c)^{8/3}$, where G is a material parameter.[6] Likewise, the decaying part of the modulus can be written $G_r(t, \epsilon_t) = G_0 \times (1 + t/\tau_0)^{-2/3} \exp(-t/\tau_z)^\beta$, where G_0 is the glassy modulus and $\beta \cong 0.4$ according to a current theory.[7] It is useful to view the growth of the equilibrium modulus as a manifestation of the "ergodicity breaking" that occurs at the gel point. At the gel point some degress of freedom take on infinite relaxation times as large clusters attach to the infinite network. In fact, there is just one infinite mode per correlation volume in the postgel regime.

Boltzmann Superposition. Before discussing stress calculations for materials with a time-dependent modulus, it is helpful to briefly consider the time-independent case. When a viscoelastic material is deformed by some appropriately defined unit amount, the equipartition principle tells us that ~kT of energy is stored in each normal mode. Noting that the glassy modulus is an energy density, the normal-mode density is then just G_0/kT. Some time t later, many of these normal modes will have relaxed, the density of unrelaxed normal modes is $G(t)/kT$, since only the unrelaxed modes contribute to the stress. At infinite time the stress is proportional to the equilibrium modulus, so the density of modes with infinite relaxation times is G_∞/kT.

To compute the stress that results from a time-dependent strain, suppose a sample has been deformed at various discrete times t_k until some final time t_f. In terms of the relaxation modulus $G(t)$, the stress that is due to the memory of the initial, undeformed state is $G(t_f-t_0)\,[\gamma(t_f)-\gamma(t_0)]$, where $G(t_f-t_0)/kT$ is the memory of the initial state in terms of the unrelaxed mode density and $\gamma(t_f)-\gamma(t_0)$ is the strain relative to the initial state. Likewise, the stress $\sigma_1(t_f)$ due to the memory of the first deformed state is then $[G(t_f-t_1)-G(t_f-t_0)][\gamma(t_f)-\gamma(t_1)]$, where *at the time* t_1 *of the first deformation*, $[G(t_f-t_1)-G(t_f-t_0)]/kT$ is proportional to the density of relaxed modes (the unrelaxed modes contribute to the stress due to the initial state). The stress contribution from the second deformed state includes only those modes that have relaxed at t_2, etc., so the contribution to the stress at time t_f from the kth state is

$$\sigma_k(t) = [G(t_f-t_k) - G(t_f-t_{k-1})][\gamma(t_f) - \gamma(t_k)] \qquad (5)$$

Collecting terms of order $G(t_f-t_k)$ (i.e, integrating by parts) gives the differential form $G(t_f-t_k)[\gamma(t_{k+1})-\gamma(t_k)]$ and summing in the continuum limit leads to the Boltzmann superposition relation[5]

$$\sigma(t) = \int_0^t \mathrm{d}s\, G(t-s)\, \dot{\gamma}(s) \qquad (6)$$

It will later prove useful to think of the stress as the zero-time (glassy) modulus times an effective strain, $\sigma(t) = G_0\gamma_{\text{eff}}(t)$, where $\gamma_{\text{eff}}(t)$ is

$$\gamma_{\text{eff}}(t) = \int_0^t \mathrm{d}s\, \dot{\gamma}(s)\, \Gamma(t-s) \qquad (7)$$

and $\Gamma(t-s) = G(t-s)/G_0$. Although this seems trivial, it will be helpful in understanding the constitutive equation for stress development during cure.

Constitutive Equation for Cure Stresses. Beyond the gel point, it is tempting to simply substitute the time-dependent modulus into eq 6. However, this begs the question of whether to use the *deformation-time* shear relaxation modulus, $G(t-s,\epsilon_s) = G_r(t-s,\epsilon_s) + G_\infty(\epsilon_s)$, or the *current-time* relaxation modulus, $G(t-s,\epsilon_t)$. If the deformation-time relaxation modulus is used, two problems arise. First, the decaying contribution to the stress, $\sigma_r(t)$, will include long relaxation times due to strain deformations that occurred near the gel point. Since the fluid no longer contains these long relaxation times (they now contribute to the equilibrium modulus), it is unphysical to include them in the relaxing part of the stress. Second, the equilibrium contribution $\sigma_\infty(t)$ to the stress would be given by eq 1, which *underestimates* the equilibrium stress since it neglects memory effects.

If instead the current-time modulus is used, then the decaying contribution is expressed only in terms of the relaxation times that still exist, so

$$\sigma_r(t) = \int_0^t \mathrm{d}s\, G_r(t-s,\epsilon_t)\, \dot{\gamma}(s) \qquad (8)$$

However, the equilibrium contribution to the stress is now given by eq 2, which *overestimates* the equilibrium contribution since it assumes complete memory of all previous states. The equilibrium term thus deserves special consideration.

The coupling of the viscoelastic memory to the equilibrium elastic stress is an exercise in careful bookkeeping. The appropriate question is as follows: What is the contribution $\sigma_k(t_f)$ to the equilibrium stress at time t_f from the cross-linking that occurred in the time interval $[t_{k-1}, t_k]$? This differential contribution is itself a sum over all prior times $t_i \le t_k$. For example, the contribution from the strain state at time t_0 is $[G_\infty(t_k) - G_\infty(t_{k-1})][\gamma(t_f)-\gamma(t_0)]\cdot\Gamma_r(t_k-t_0,\epsilon(t_k))$. The first two terms are obvious: $G_\infty(t_k) - G_\infty(t_{k-1})$ is the modulus increment from t_{k-1} to t_k, and $\gamma(t_f) - \gamma(t_0)$ is the overall strain relative to the initial state. The third term, $\Gamma_r(t_k-t_0,\epsilon(t_k)) = G_r(t_k-t_0,\epsilon(t_k))/G_r(0,\epsilon(t_k))$, is the memory of the initial state during the time of the equilibrium modulus increment. This couples the relaxing stresses to the equilibrium stresses.

Likewise, the contribution to $\sigma_k(t_f)$ from the strain state at time t_i is

$$\sigma_{ik}(t_f) = [G_\infty(t_k) - G_\infty(t_{k-1})][\gamma(t_f) - \gamma(t_i)] \times [\Gamma_r(t_k-t_i,\epsilon(t_k)) - \Gamma_r(t_k-t_{i-1},\epsilon(t_k))] \qquad (9)$$

Thus the memory term only includes those modes that have not already been attributed to the strain state at time t_{i-1}. Summing these contributions and taking the continuum limit gives

$$\sigma_\infty(t) = \gamma(t)\, G_\infty(\epsilon_t) - \int_0^t \mathrm{d}s\, G_\infty'(\epsilon_s) \int_0^s \mathrm{d}u\, \gamma(u) \frac{\mathrm{d}}{\mathrm{d}u}\Gamma_r(s-u,\epsilon_s) \qquad (10)$$

Since the double integral is nonnegative, the strong memory term $\gamma(t)\,G_\infty(\epsilon_t)$ appears as an *upper limit* to the equilibrium stress, as we have shown in eq 2. From eq 10 we observe that this upper limit is realized only when the time derivative of the decaying part of the modulus is zero, i.e., when the system has complete memory.

Alternatively, integration by parts yields an expression with a transparent physical interpretation

$$\sigma_\infty(t) = \int_0^t \mathrm{d}s\, G_\infty(\epsilon_s)\, \dot{\gamma}(s) + \int_0^t \mathrm{d}s\, G_\infty'(\epsilon_s) \int_0^s \mathrm{d}u\, \dot{\gamma}(u)\, \Gamma_r(s-u,\epsilon_s) \qquad (11)$$

The convolution integral now has the form of the Boltzmann superposition relation, so in analogy with eq 7 we can define the effective strain for a time-dependent fluid

$$\gamma_{\text{eff}}(t) = \int_0^t \mathrm{d}s\, \dot{\gamma}(s)\, \Gamma_r(t-s,\epsilon_s) \qquad (12)$$

Equation 11 is then seen to be a statement that the equilibrium elastic stress increment at time t is

$$\delta\sigma_\infty(t) = G_\infty(\epsilon_t)\, \delta\gamma(t) + \gamma_{\text{eff}}(t)\, \delta G_\infty(\epsilon_t) \qquad (13)$$

Thus, our original differential for complete memory, $\delta\sigma_\infty(t) = G_\infty(\epsilon_t)\,\delta\gamma(t) + \gamma(t)\,\delta G_\infty(\epsilon_t)$, has been modified by replacing $\gamma(t)$ by the effective strain, $\gamma_{\text{eff}}(t)$. In the limit of strong memory the effective strain equals the actual strain, giving $\sigma_\infty(t) = \gamma(t)\,G_\infty(\epsilon_t)$, and in the limit of no memory the effective strain is zero, leading to eq 1.

Finally, it is instructive to quantify memory effects through the function

$$M(t) = \frac{\sigma_\infty(t) - \sigma_\infty^{\min}(t)}{\sigma_\infty^{\max}(t) - \sigma_\infty^{\min}(t)} \qquad (14)$$

where the superscripts denote the minimum (eq 1) and maximum (eq 2) possible equilibrium stresses. $M(t) = 1$ when memory effects are large and $M(t) = 0$ in the absence of memory. From eqs 11 and 12 we observe that the memory function can then be expressed in terms of the effective strain through

$$M(t) = \frac{\int_0^t \mathrm{d}s\, G_\infty'(\epsilon_s)\, \gamma_{\mathrm{eff}}(s)}{\int_0^t \mathrm{d}s\, G_\infty'(\epsilon_s)\, \gamma(s)} \qquad (15)$$

In the next section, this function will be computed for a simple model.

In summary, the stresses induced during cure are a sum of the relaxing component of eq 8 and the equilibrium contribution given in eq 11. The equilibrium contribution is coupled to the viscoelastic memory via the effective strain of eq 12. This effective strain is a measure of the viscoelastic memory a material has.

A Model System. To better appreciate these results, it is helpful to construct a simple example, without regard to its applicability to any real system. For the relaxing component of the modulus we choose the minimal form $G_r(t) = (\eta/\tau)e^{-t/\tau}$, where η is a viscosity and τ is a relaxation time that is independent of the extent of reaction (the glassy modulus is then just $G_0 = G_\infty + \eta/\tau$). Although in a real curing system $G_r(t)$ is dependent on the extent of reaction, this approximation is sufficient to illustrate the coupling of equilibrium and relaxing stresses. If the reaction kinetics are exponential, the strain relative to the gel point is $\gamma(t) = \gamma_f(1 - e^{-t})$ where γ_f is the final strain in the fully cured system (note that the strain relaxation time is our unit of time). Likewise, the equilibrium modulus can be chosen as $G_\infty(t) = G_f(1 - e^{-t})$, which amounts to a linear increase in the modulus beyond the gel point, $G_\infty \sim |\epsilon - \epsilon_c|$, which is a much weaker dependence than the percolation result $G_\infty \sim |\epsilon - \epsilon_c|^{8/3}$. Note that, in this minimal example, the ratio of the maximum (eq 2) to minimum (eq 1) possible equilibrium stress is 2.

The memory function can be computed from eqs 12 and 15, with the result

$$M(t) = \frac{2\tau}{1+\tau}\left[1 - \frac{\tau}{1+2\tau}\,\frac{(1 - e^{-(1+2\tau)t/\tau})}{1 - e^{-t}}\right]/(1 - e^{-t}) \qquad (16)$$

Expanding the exponentials gives $M(0) = 1$, demonstrating that at early times memory effects dominate, no matter how rapid the viscoelastic decay. At large times one obtains $M(\infty) = 2\tau/(1 + 2\tau)$, showing that memory effects become very small for rapid viscoelastic decays. In the limit of long viscoelastic relaxations $M(\infty) = 1$, whereas for $\tau \ll 1$, $M(\infty) \sim 2\tau$. The behavior of the memory function is shown in Figure 1 as a function of the reduced strain, $\gamma_R(t) = \gamma(t)/\gamma_f$, for a variety of τ. In Figure 2 the reduced equilibrium stress, $\sigma_\infty(t)/G_f\gamma_f$, is plotted against the reduced strain for the same values of τ. Finally, the time dependence of the reduced stress is in Figures 3 and 6. These calculations illustrate the importance of a slow cure in minimizing cure-induced stresses.

To provide a basis of comparison, the relaxing part of the stress, calculated from eq 8, is shown in Figure 4. Here we have normalized by the maximum possible relaxing *elastic* stress, $(G_0 - G_\infty)\gamma(t)$. Although the maximum *reduced* stress occurs initially, at long times the stress decays to zero, as it must. It is more instructive to normalize the decaying stress by the *viscous* stress $\eta\gamma'(t)$, as shown in Figure 5. When the viscous relaxations are faster than the strain rate, the fluid acts like a viscous fluid, as indicated by the constant behavior of the normalized stress at large strains. However, when the viscous relaxations are slower, $\tau > 1$, the reduced stress (not the true stress!) diverges at maximum strain, indicating significant residual energy storage in the fluid. At the crossover ($\tau = 1$) from viscous-like behavior, the divergence is logarithmic, $\sigma_r(t)/\eta\gamma' = -\ln(1 - \gamma_R)$; however, for larger values of τ the divergence is of the power law form $\sigma_r(t)/\eta\gamma'(t) = 1/[(\tau - 1)(1 - \gamma_R)^{1-1/\tau}]$.

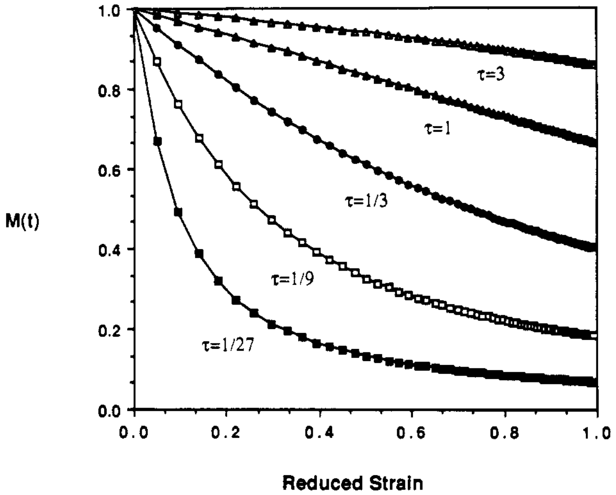

Figure 1. Memory function, $M(t)$, plotted against the reduced strain, $\gamma_R(t) = \gamma(t)/\gamma_f$, for a curing material with a single relaxation time τ, where the unit of time is the reaction time, and the strain is assumed to follow the chemical reaction. Although strong memory effects are observed initially, regardless of the viscoelastic relaxation time, at longer times and larger strains there is a significant loss of memory for fast viscoelastic relaxations, i.e., $\tau \ll 1$.

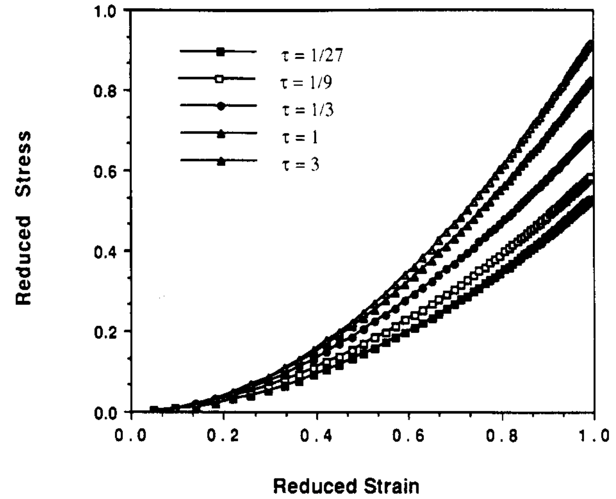

Figure 2. Reduced equilibrium stress, $\sigma_\infty(t)/G_f\gamma_f$ shown as a function of the reduced strain for the simple, single relaxation time model. Note that since in this model the modulus is proportional to the extent of reaction beyond the gel point, these curves are quadratics in the short and long memory limits. The large stresses that occur for the longest relaxation times τ are a result of the strong memory effects shown in Figure 1. Note that with $\tau = 3$ the reduced equilibrium stress approaches the maximum possible value of 1.

Discussion

A number of practical difficulties arise in applying these constitutive equations to real systems. For instance, there are substantial data reduction problems, as well as some delicate issues concerning the glassy modulus. Thus it seems worthwhile to discuss these issues briefly.

Time–Cure Superposition. In principle, it is probably best to directly measure both the volume relaxation and the viscoelastic functions as a function of the extent of reaction. However, this can be a daunting, tedious task, and the amount of data thus produced can be truly stunning. Also, for rapid cures it is difficult to actually

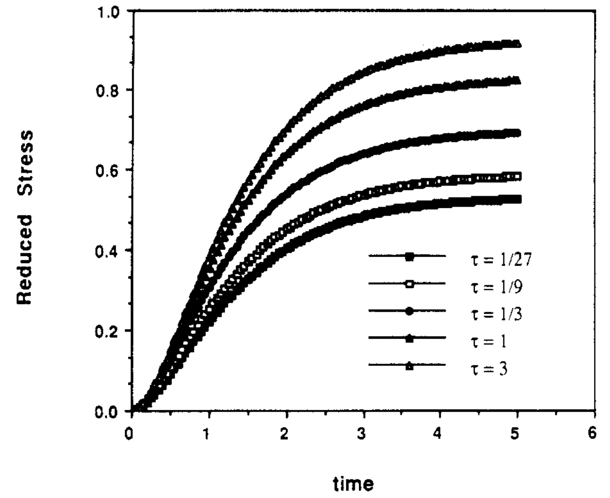

Figure 3. Reduced equilibrium stress shown, in order to give a semblance of real data, as a function of time for the exponential model. Since the modulus can change significantly with small increases in the extent of reaction, substantial increases in the equilibrium stress can occur in the regime where the cure shrinkage is essentially unmeasurable.

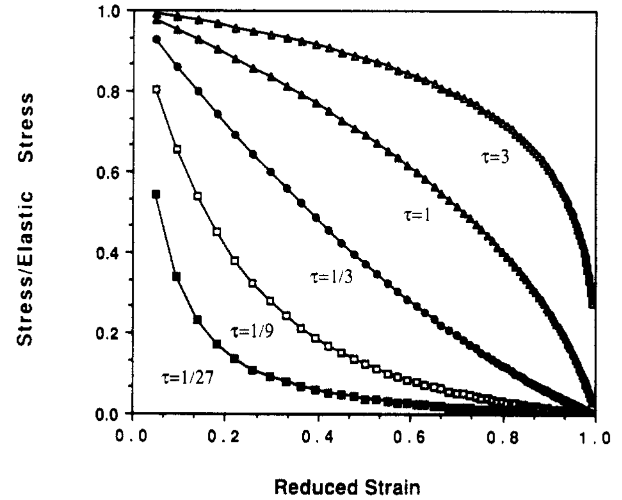

Figure 4. Decaying, nonequilibrium contribution to the stress plotted against the reduced strain for the simple case of a viscoelastic material with a single relaxation time (compare Figure 2). Here the stress is normalized by the maximum possible nonequilibrium *elastic* stress $(G_0 - G_\infty)\gamma(t)$, so that the reduced stress is bounded by unity. This then provides a measure of the loss of memory at large times, since in the long memory limit the reduced stress would be unity for all values of the reduced strain less than 1.

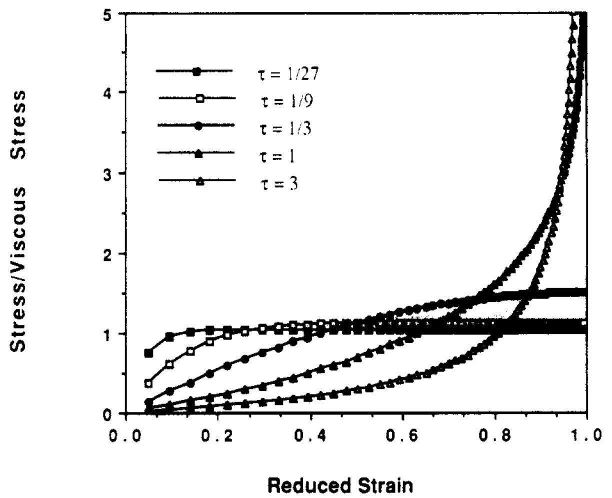

Figure 5. Decaying, nonequilibrium contribution to the stress (Figure 4) normalized by the *viscous* stress $\eta\gamma'(t)$ for the slowly relaxing samples with $\tau > 1$ shown as a power law divergence, $\sigma_r(t)/\eta\gamma'(t) \sim 1/(1 - \gamma_R)^{1-1/\tau}$ at large times. This implies that in these slowly relaxing samples the viscous dissipation occurs at a rate that is insufficient to keep up with the elastic energy storage accompanying strain.

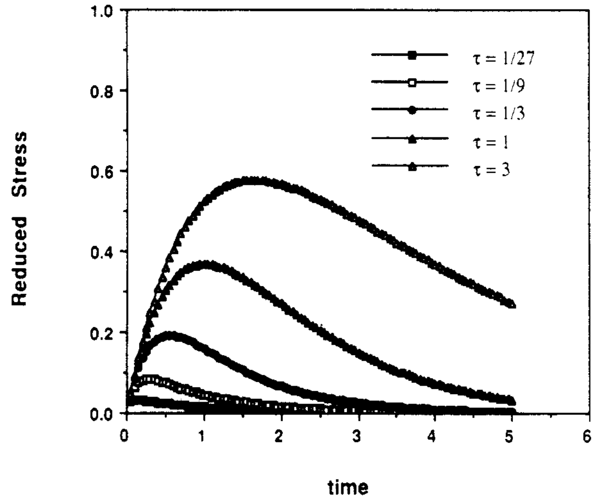

Figure 6. Reduced nonequilibrium stress shown, in order to give a semblance of real data, as a function of time for the exponential model. These data should be compared to those in Figure 3 for the equilibrium stress. Note that since the glassy modulus is typically much larger than the equilibrium modulus, the nonequilibrium contribution to the stress can be substantial. However, in a slowly curing material the nonequilibrium stresses become negligible and the equilibrium stresses dominate.

measure the viscoelastic functions on a time scale that is sufficiently short that material properties do not change. When so confronted, one often finds theoretical results helpful in reducing the data to a simple functional form having a few material parameters. In this regard, the recent experimental and theoretical work cited in the references is most helpful, but we still feel the following comments are in order.

The most useful theoretical result is *time–cure superposition*,[11] which states that near the gel point the time- or frequency-dependent viscoelastic functions form universal curves on dimensionless axes where the modulus is scaled by the equilibrium modulus and the time or frequency is scaled by the longest relaxation time τ_z. Thus the full gel point behavior can be constructed by measuring viscoelastic properties at a single extent of reaction. This is quite analogous to *time–temperature superposition*,[5] where viscoelastic data taken at a variety of temperatures can be plotted universally if the temperature dependence of the friction is known. In the case of time–cure superposition the situation is somewhat better, since the "shift factors" for each axis are known universal power laws of the extent of reaction.

Far beyond the gel point the situation is more complex, since universal power laws and time–cure superposition are not expected to apply. However, the extent of the critical regime is surprising, so it is really only in the very latest stages of cure that direct viscoelastic measurements must be performed. The late stages also pose another difficulty; since the deformation moduli are large, even small volume relaxations can create large stresses. These small volume changes are difficult to measure, so large computational uncertainties can arise at large times.

Glassy Modulus. To define the effective strain for a fluid with time-dependent viscoelastic properties, it was necessary to normalize the relaxation modulus by the short-time, or glassy, modulus, G_0. In fact, the appropriate normalization is a nontrivial matter, so this point deserves some discussion. When a sample beyond the gel point is subjected to an oscillating strain, the storage part $G'(\omega)$ of the complex modulus increases with frequency ω. At the lowest frequencies, entropy is stored only in the "elastic" network, and $G'(\omega) \cong G_\infty$. When the frequency exceeds $1/\tau_z$, where τ_z is the longest Rouse mode in the material, entropy is stored by affinely deforming modes with relaxation times longer than $1/\omega$. Finally, at a frequency of $\omega_0 \cong 1/\tau_0$, where τ_0 is the decay time of the fastest Rouse mode, the deformation will become affine on all length scales down to the Kuhn length. Since higher frequencies would store both enthalpy and entropy in local deformations on length scales smaller than the Kuhn length, this would be the highest frequency where one would expect time-temperature superposition to apply. Stress-temperature studies show that the equilibrium modulus is entropic in origin, so we believe $G'(\omega_0)$ to be the appropriate "glassy" modulus with which to normalize the relaxation modulus. This modulus is smaller than the glassy modulus just beyond the α transition and may be operationally defined as the modulus at the high frequency end of the power law dependence, $G'(\omega) \sim \omega^\Delta$.

Conclusions

When a viscoelastic material cures, both equilibrium and nonequilibrium stresses can arise. If these stresses exceed the strength of the material, cracking or plastic deformation will occur. We have shown that during cure there are two possible contributions to the incremental equilibrium stress $\delta\sigma_\infty(t)$: the first contribution is the product of the incremental strain and the equilibrium modulus, $G_\infty(\epsilon_t)\,\delta\gamma(t)$; the second contribution is the product of the *effective* strain times the incremental modulus, $\gamma_{\text{eff}}(t)\,\delta G_\infty(\epsilon_t)$. The effective strain depends on the deformation history of the sample and can be as small as zero in the limit of a very slow cure or as large as the true strain in the limit of a very fast cure. Since this second term can be at least as large as the first term, a slow cure cycle is desirable if equilibrium cure stresses need to be minimized. A slow cure also minimizes the development of relaxing stresses, thus reducing the possibility of failure.

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