Stress–Relaxation in Three-Element and Four-Element Mechanical Models of Viscoelastic Materials

DONALD D. JOYE

Department of Chemical Engineering, Villanova University, Villanova, Pennsylvania 19085

SYNOPSIS

Three- and four-element mechanical analogues are commonly used to describe viscoelastic behavior in creep (deformation under constant force or stress) but not in stress relaxation (stress response after a suddenly imposed, constant strain). Mathematical models of the mechanical analogues in stress–relaxation are re-derived in this work, keeping notation familiar to polymer scientists. The relationship is shown to meet consistency tests and predicts, with very good accuracy, the behavior of a polyisobutylene sample in stress relaxation when the equation constants were derived from creep experiments. In experiments on an actual mechanical analog, the motion of the Voigt element is shown to exhibit a maximum stress. Implications for the interpretation of creep and stress–relaxation data on the same material are discussed. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Mechanical analogues are useful constructs in the description of viscoelastic behavior and are treated in some detail in almost all polymer and rheology textbooks (e.g., refs. 1–6). A viscoelastic fluid can be modeled accurately by the so-called four-element model, whereas a viscoelastic solid is often described in terms of a three-element model, which is the four-element model minus the long-term viscous component.

The predictions of these models for creep (deformation–time response of a material under constant load or stress) are easily derived and clearly applied. Thus, these models have found common use in describing the viscoelastic behavior of polymers, composites, foodstuffs, and other like materials in creep. The predictions of these models in a stress–relaxation test have been known for some time in the mechanics area,[7,8] but the derivations and notation have created barriers to their use in the polymer field. Instead, the generalized Maxwell model has been recommended for interpretation of stress-relaxation data. This bears no relation to creep, and a potentially valuable cross reference is lost. Some practitioners may be unhappy with the infinite complexity of the generalized model and are unsure of the physical significance of its constants.

The four-element model and its three-element counterpart are convenient engineering models of viscoelastic behavior because of their relative simplicity and their fundamentally correct representation of real behavior.[9] It would be useful to have a working model for stress-relaxation tests.

In this work the governing differential equations are solved by LaPlace transforms, keeping notation of common understanding and physical interpretation in polymer rheology. The resulting predictions in stress relaxation are tested with an actual mechanical model of springs and dashpots and with a real material in which both creep and stress relaxation data had been obtained.

THEORY

The four-element model is a series combination of a Maxwell model (elastic and viscous elements in series) and a Voigt model (elastic and viscous elements in parallel) and is shown in Figure 1. The standard notation for the Maxwell elements (E_1 for the Hookean, linear elastic modulus, and η_3 for the Newtonian viscosity) and the Voigt elements (E_2

Journal of Applied Polymer Science, Vol. 47, 345–350 (1993)
 CCC 0021-8995/93/020345-06

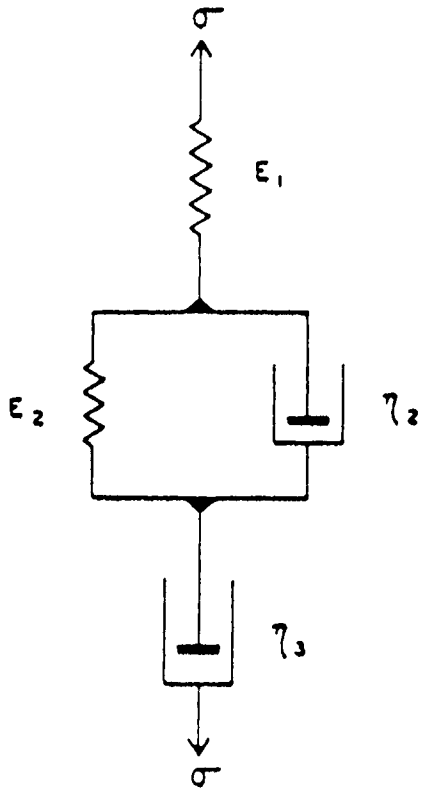

Figure 1 Schematic representation of the four-element model.

and η_2) is used. Hooke's law is used for the elastic modulus,

$$\sigma = E\epsilon \tag{1}$$

and Newton's law for the viscosity.

$$\sigma = \eta d\epsilon/dt \tag{2}$$

Thus, the four-element model usually is described as a linear viscoelastic model.

In a stress relaxation test the mechanical model (or real material) is stretched or otherwise deformed from an initial rest state to a fixed strain for all time thereafter, during which the stress response is measured. The stress decays from a maximum at time zero owing to the viscous rearrangement of chains in a polymeric material, for example, or to the viscous extension of a shock absorber (dashpot) in the mechanical analog. The viscous elements are strain-rate dependent, not strain dependent as are the elastic elements.

During stress relaxation each element experiences the same stress, because the elements are in series (the electrical analogy works well here). However, the two elements of the Voigt component (subscript "2" in Fig. 1) are coaxial and attached to each other at both ends, and therefore experience the same strain at all times. Each element of the Voigt component may or may not carry the same stress, but the component as a whole will be subject to the same stress as the Maxwell spring (E_1) and the Maxwell dashpot (η_3).

In stress relaxation each element (Maxwell spring, Voigt component, and Maxwell dashpot) experiences a different strain, but the strains are additive to produce the total strain. Thus,

$$\frac{d\epsilon_{\text{tot}}}{dt} = \frac{1}{E}\frac{d\sigma}{dt} + \frac{\sigma}{\eta} + \frac{d\epsilon_v}{dt} \tag{3}$$

where ϵ_v is the strain in the Voigt component. After the step increase in strain in a stress-relaxation test, $d\epsilon_{tot}/dt = 0$.

The strain rate term for the Voigt component can be derived from its governing equation for stress:

$$\sigma(t) = \epsilon_v E + \eta d\epsilon_v/dt \tag{4}$$

which can be rearranged to read,

$$d\epsilon_v/dt = \sigma(t)/\eta - \epsilon_v E/\eta \tag{5}$$

and substituted into eq. (3), with appropriate subscripts for the model,

$$0 = \frac{1}{E_1}\frac{d\sigma}{dt} + \frac{\sigma(t)}{\eta_3} + \frac{\sigma(t)}{\eta_2} - \epsilon_v\frac{E_2}{\eta_2} \tag{6}$$

The strain in the Voigt component is also a function of time and needs to be represented without reverting to eq. (5) or circularity. If the LaPlace transform method is used,[10,11] one can more easily see a way to solution. The LaPlace transform of eq. (5) is,

$$s\epsilon_v(s) - [d\epsilon_v/dt]_0 - \sigma(s)/\eta_2 - \epsilon_v(s)E_2/\eta_2 \tag{7}$$

The boundary condition for strain at time zero for the Voigt component is zero. Therefore,

$$(s + 1/\tau_2)\epsilon_v(s) = \sigma(s)/\eta_2 \tag{8}$$

or

$$\frac{\epsilon_v(s)}{\sigma(s)} = \frac{1/\eta_2}{(s + 1/\tau_2)} \tag{9}$$

This is valid for the instantaneous strain in response to instantaneous stress. No lag exists between the two because of the coaxial nature of the Voigt component. The time inverse of eq. (9) is an exponential; if the stress is constant, we have the familiar Voigt expansion. But in a stress–relaxation test, the stress is decaying. Therefore, the immediate response, where the stress is largest, will be to expand rapidly; but as the stress decays, the Voigt component will tend to retract. Thus, eq. (9) suggests that the Voigt component of the four-element model will go through a maximum. That is, the Voigt component should expand first, then contract during a stress relaxation test.

We proceed to a general solution by taking the LaPlace transform of eq. (6),

$$0 = (1/E_1)(s\sigma(s) - \sigma_0) + (1/\eta_2 + 1/\eta_3)\sigma(s) - (E_2/\eta_2)\epsilon_v(s) \quad (10)$$

The stress at time zero (σ_0) is not zero here, rather it will be a maximum. Substituting eq. (9) into eq. (10) and rearranging gives,

$$\frac{\sigma_0}{E_1} = \sigma(s)\frac{s}{E_1} + \frac{1}{\eta_3} + \frac{1}{\eta_2} - \frac{1}{\tau_2\eta_2} \times \frac{1}{(s + 1/\tau_2)} \quad (11)$$

where $\tau_2 = \eta_2/E_2$. Note that in eq. (7) the initial strain in the Voigt component is zero upon imposition of stress (the Voigt component responds in a viscous rather than an elastic fashion). In contrast, the four-element model responds immediately to sudden imposition of strain, showing a non-zero initial stress as in eq. (11), because of the Maxwell spring (E_1) response.

Rearranging eq. (11) for inversion to the time domain,

$$\sigma(s) = \frac{\sigma_0}{s + E_1(1/\eta_3 + 1/\eta_2) - \dfrac{E_1/\tau_2\eta_2}{(s + 1/\tau_2)}} \quad (12)$$

which can be further rearranged to

$$\sigma(s) = \frac{\sigma_0(s + 1/\tau_2)}{(s + 1/\tau^*)(s + 1/\tau_2) - 1/\tau_2\tau_{21}} \quad (13)$$

where

$$\tau^* = (1/\tau_{31} + 1/\tau_{21})^{-1} \quad (14)$$

and

$$\tau_{31} = \eta_3/E_1 \quad (15)$$

$$\tau_{21} = \eta_2/E_1 \quad (16)$$

Note the cross time constants here.

Equation (13) can be inverted by partial fraction expansion according to known methods.[10,11] The solution has the form,

$$\sigma(t) = \sigma_0[A_1\exp(r_1t) + A_2\exp(r_2t)] \quad (17)$$

where A_1 and A_2 are constants determined from the partial fraction inversion, and r_1 and r_2 are the roots of the quadratic equation in the denominator of eq. (13). Equation (13) can be rewritten in general form for partial fraction expansion as follows:

$$\frac{s + 1/\tau_2}{(s - r_1)(s - r_2)} = \frac{A_1}{s - r_1} + \frac{A_2}{s - r_2} \quad (18)$$

Isolating A_1 by multiplying both sides of eq. (18) by the denominator of A_1, then setting $s = r_1$, yields

$$A_1 = (r_1 + 1/\tau_2)/(r_1 - r_2) \quad (19)$$

and by analogy,

$$A_2 = (r_2 + 1/\tau_2)/(r_2 - r_1) \quad (20)$$

The denominator of eq. (13) can be found by multiplying out the terms and collecting like powers of "s",

$$\text{denom.} = s^2 + (1/\tau^* + 1/\tau_2)s + (1/\tau_2)(1/\tau^* - 1/\tau_{21}) \quad (21)$$

The quadratic formula, $[-b \pm \sqrt{(b^2 - 4ac)}]/2a$, can be used to find the roots r_1 and r_2, and since $1/\tau^* - 1/\tau_{21} = 1/\tau_{31}$,

$$r_1, r_2 = -(1/\tau^* + 1/\tau_2)/2 \pm \sqrt{[(1/\tau^* + 1/\tau_2)^2/4 - 1/\tau_2\tau_{31}]} \quad (22)$$

The solution must be real, so both roots must be negative. Thus, r_1 may be taken as the root with the positive sign in front of the square root term in eq. (22) and r_2 the root with the negative sign. This means the solution is a complicated expression comprising the sum of two exponential decay terms with mixed time constants. Thus the equation for the four-element model in stress relaxation is eq. (17), where r_1 and r_2 are negative roots found from eq. (22), and A_1 and A_2 are found from eqs. (19) and (20), respectively.

DISCUSSION

Predicting Stress Relaxation of a Polymer

The theory can be used to predict the stress–relaxation response of a real material when the constants have been obtained from a creep test. For Vistanex L-80 polyisobutylene at room temperature, data from independent tests on the same material are available.[12] Stress–relaxation data were obtained by the Gehman apparatus, which uses a torsional deformation, and biaxial creep data were obtained by a bubble inflation apparatus described in the reference. At low deformations ($\leq 70\%$), the elasticity of Vistanex L-80 is Hookean. Unfortunately, the viscosity is non-Newtonian to quite low rates of deformation. Thus for fair comparison, the deformation rates or equivalent times must be matched relatively closely with the times and deformations of the stress–relaxation test in the Gehman apparatus.

From Figure 21 in ref. 12, the following constants for the four-element model representation of the creep curve were obtained:

$$E_1 = 1.6 \times 10^7 \text{ dyn/cm}^2,$$

$$E_2 = 2.1 \times 10^7 \text{ dyn/cm}^2,$$

$$\eta_3 = 1.4 \times 10^{10} \text{ P, and}$$

$$\eta_2 = 2.4 \times 10^8 \text{ P.}$$

The four-element model in stress relaxation then has the following constants: $\tau_{31} = 875$ s, $\tau_{21} = 15$ s, $\tau_2 = 11.4$ s, $A_1 = .566$, and $A_2 = .434$. For the two exponential decay terms, $r_1 = -.0004$ and $r_2 = -.1546$.

The stress–relaxation data (corrected to 23°C from 20°C) is compared with the predictions of eq. (17) in Figure 2. The fit is quite close. The theory appears to predict slightly faster relaxation in the early stages; however, this may be due to inaccuracies in the estimate of τ_2 from the creep data (this is the constant with the least accuracy).

Traditional interpretation of the long-time portion of the stress-relaxation curve would give a time constant of 2450 s, which clearly is not equivalent to the long-term time constant in the creep test (as may be commonly assumed). But the theory shows that it should not be. The long-time behavior of the four-element model in stress relaxation is governed by all three time constants, only one of which is the Maxwell element time constant (τ_{31}). The other is the Voigt component time constant (τ_2), and the third is a cross value between the Voigt dashpot and the Maxwell spring (τ_{21}). The theory predicts no interaction between the Maxwell dashpot and the Voigt component (there is no τ_{32}).

The dominant exponential is the A_1 term, which has a very small root, therefore accuracy in calculating the roots, especially the one close to zero, is very important.

What is the role of the Voigt component in stress relaxation? It is commonly assumed in thinking about viscoelasticity, that the Voigt response governs the short-time relaxations, as it does in creep. This depends on the relative value of the time constants, but appears to be generally true for most real materials. The assumption goes further, however, and says that once the Voigt response is over (following the creep behavior) then the long-time response is governed by the Maxwell element alone. This is true in creep but is clearly not true in the stress relaxation of a four-element model. Figure 2 implies the Voigt response is never quite finished; it goes through a maximum and still shows some response at long time. The theory shows this by including Voigt component time constants in the roots. If the Voigt component were frozen (η_2 = infinity, hence τ_2's are also infinity), then the equation for the roots shows $r_1 = 0$ and $r_2 = -1/\tau_{31}$, and $A_1 = 0$ and $A_2 = 1.0$. This gives single exponential behavior with a Maxwell element time constant. Thus, the theory matches expectations for this case. It seems highly unlikely in a real material that the Voigt component would ever be frozen out, and consequently one has the complex long-time behavior shown by both the theory and a real material (such as Vistanex L-80 in Fig. 2). As long as there is stress, the Voigt component will be responding: its response will not disappear until the stress does. Long-time relaxation, then, cannot be the relaxation of a purely Maxwell element. This also says one cannot get relaxation times from a stress relaxation test, if the four-element model is used to describe the behavior.

The Viscoelastic Solid

A viscoelastic solid is often modeled by a three-element derivative of the four-element model. Take away the Maxwell dashpot and one has a three-element model capable of predicting responses in a viscoelastic solid [i.e., a material without a long-term viscous response (flow)]. Cross-linked polymers fall into this category.

The creep response of such a model is well known, viz. a sudden purely elastic response, followed by a

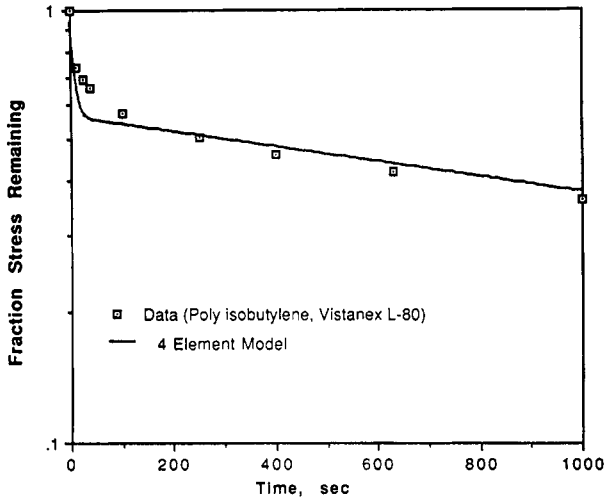

Figure 2 Stress relaxation of Vistanex L-80 at 23°C (data points) compared with the predictions of the four-element model equation in stress relaxation with the constants determined in creep.

rising exponential of the form $1 - \exp(-t/\tau)$ to a limiting, asymptotic strain or deformation. What does the theory predict for stress relaxation of the same material? Clearly the stresses should not relax to zero.

Solving eqs. (17), (19), (20), and (22) with $\tau_{31} = \infty$ gives $r_1 = 0$, $r_2 = -(1/\tau_{21} + 1/\tau_2)$, $A_1 = E_1/(E_1 + E_2)$ and $A_2 = E_2/(E_1 + E_2)$. This yields the response curve shown in Figure 3. The time response is governed not solely by the Voigt time constant, τ_2, but by a combination of that with a cross time constant involving the Voigt viscous element and the Maxwell spring (τ_{21}). The long-time behavior shows constant residual stress, as expected. The fraction of original stress remaining is given by A_1. The time it takes to reach that state may be reasonably approximated by 5 to 7 time constants, where the time constant is given by $-1/r_2$. Multiples of the time constants for Vistanex L-80 are used to show relative relaxation dependence on those values.

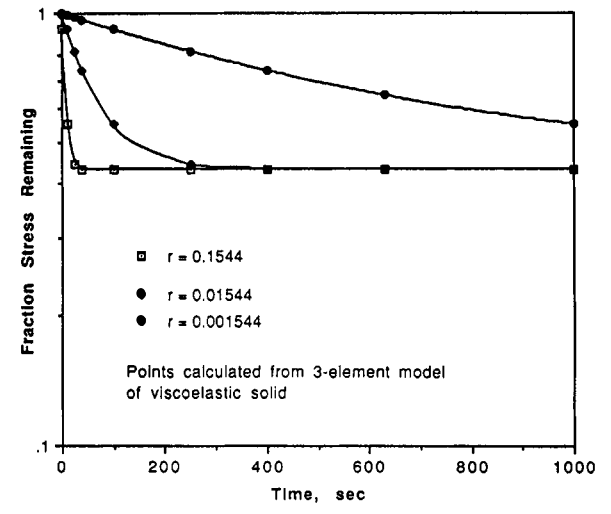

Figure 3 Prediction of stress-relaxation behavior in a three-element model of a viscoelastic solid.

Voigt Component Motion

Stress–relaxation tests were carried out on an actual mechanical model of springs and dashpots (shock absorbers) by attaching the upper, Maxwell spring to an I-beam in the ceiling and weighting the bottom of the same spring, so that the unstressed lower Voigt element and Maxwell dashpot could be attached to an eyelet embedded in the floor without stress. At time zero the weight was removed by releasing a vise-grip turnbuckle, and stress relaxation commenced. While the overall strain remained the same, the distances of the upper spring base and the lower dashpot top were measured as a function of time. Since the total distance was always the same, the distance the middle Voigt element stretched could be obtained by difference.

Typical results of this test are shown in Figure 4. Curve "S" is the length of the Maxwell spring; curve "D" is the length of the Maxwell dashpot (an automotive shock absorber in this case). The move-

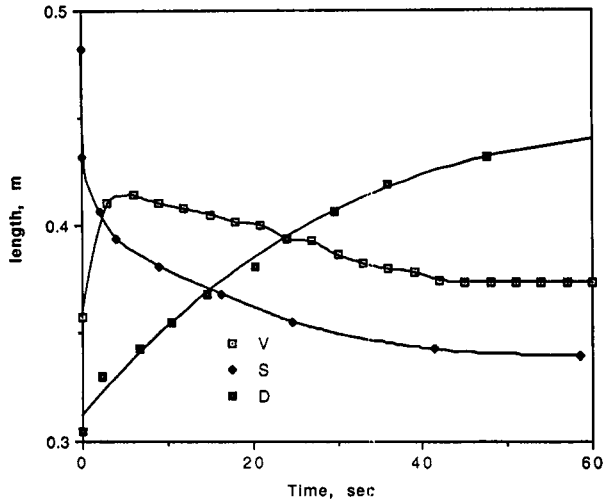

Figure 4 Relaxation in an actual mechanical analog, curve S is Maxwell spring motion, curve D is the Maxwell dashpot motion, curve V is the motion of the Voigt component.

ment of the Voigt element is shown by curve "V," which is the difference between the upper and lower curves, as it must be. The sum of the three curves at any point in time is always $1.14m \pm 0.01$. Both curves "S" and "D" show relaxation, but their difference, which is the length-time characteristic of the Voigt element, shows a maximum. This is predicted by the theory, and would not have been evident in normal testing, unless the sample were an actual mechanical model as presented here. A polymeric sample would have given only the overall stress decay curve, so the theory could not have been completely tested by this alone.

Good quantitative stress–relaxation data could not be obtained with this apparatus because of control and alignment problems resulting in extra sources of friction, such as between spring and shock absorber in the (coaxial) Voigt component, and various nonidealities in the shock absorber itself.

CONCLUSIONS

This work reinterprets the behavior of the 4-element model in stress relaxation and provides a common link between creep and stress–relaxation behavior of a single material. The three- and four-element models are relatively simple, intuitively satisfying, and generally accurate descriptors of viscoelastic behavior. The predictive ability for real viscoelastic materials is shown to be quite good. The three-element formulation shows quantitative predictions for a viscoelastic solid in stress relaxation with its unique "residual stress" reaction at long times. It has also been demonstrated that the Voigt component of a four-element model shows a maximum in deformation in stress relaxation, and that its response cannot be assumed to disappear at long times. Consequently, the long time behavior in creep and stress relaxation are not equivalent. The four-element model widely used to describe creep can now also be used to predict the stress–relaxation behavior of viscoelastic materials, uncrosslinked or crosslinked polymers, foodstuffs, pharmaceuticals, or the like.

The author thanks senior project student, John McCartney, and technician Chris Lynch for their assistance in constructing the actual mechanical analog and in data collection.

NOMENCLATURE

A = constant (dimensionless)
E = elastic modulus, σ/ϵ (dyn/cm^2)
ϵ = strain, dL/L, (dimensionlesss)
η = viscosity, $\sigma/(d\epsilon/dt)$ (P)
l = length (m)
r = root (time^{-1})
s = LaPlace domain variable (time^{-1})
σ = stress (dyn/cm^2)
t = time (s)
τ = relaxation time, η/E (s)

REFERENCES

1. R. B. Bird, R. C. Armstrong, and O. Hassager, *Dynamics of Polymeric Liquids,* vol. 1, J. Wiley & Sons, New York, 1977.
2. G. R. Moore and D. E. Kline, *Properties and Processing of Polymers for Engineers,* SPE Monograph, Prentice-Hall, Englewood Cliffs, NJ, 1984.
3. L. E. Nielsen, *Mechanical Properties of Polymers and Composites,* vols. 1 and 2, Marcel Dekker, New York, 1974.
4. P. Sherman, *Industrial Rheology,* Academic Press, New York, 1970.
5. A. V. Tobolsky, *Properties and Structure of Polymers,* J. Wiley & Sons, New York, 1960.
6. S. L. Rosen, *Fundamental Principles of Polymeric Materials,* Wiley-Interscience, New York, 1982.
7. W. Flügge, *Viscoelasticity,* 2nd ed., Springer Verlag, New York–Berlin, 1975.
8. R. Darby, *Viscoelastic Fluids: An Introduction to Their Properties and Behavior,* Marcel Dekker, New York–Basel, 1976.
9. T. Alfrey and E. F. Gurnee, Dynamics of viscoelastic behavior, in *Rheology,* vol. I, F. R. Eirich, ed., Academic Press, New York, 1956, Chap. 11.
10. D. R. Coughanowr and L. B. Koppel, *Process Systems Analysis and Control,* McGraw-Hill, New York, 1965.
11. V. G. Jenson and G. V. Jeffries, *Mathematical Methods in Chemical Engineering,* Academic Press, New York, 1963.
12. D. D. Joye, "A Bubble Inflation Technique for the Measurement of Viscoelastic Properties in Equal Biaxial Extensional Flow," Ph.D. thesis, Department of Chemical Engineering, Lehigh University, Bethlehem, PA, 1972. Available through University Microfilms, Ann Arbor, MI.

Received December 16, 1991
Accepted March 3, 1992