JOURNAL OF MATERIALS SCIENCE 20 (1985) 1920–1928

Constitutive equations of ageing polymeric materials

S. T. J. PENG
Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California, USA

In a previous paper, a constitutive equation of relaxation behaviour of time-dependent chemically unstable materials has been developed by employing the irreversible thermodynamics of internal variables and Eyring's absolute reaction theory. In that paper, a theoretical expression for the effect of chemical crosslink density, ν, on the relaxation rate has been developed. In this paper the creep behaviour of a network polymer undergoing a scission process has been developed. The temperature effect using the WLF equation on the coupled chemomechanical behaviour has also been incorporated into the equation.

1. Introduction

In a previous paper [1], a general constitutive equation of relaxation behaviour of time-dependent chemically unstable materials has been developed by employing the irreversible thermodynamics of internal variables and Eyring's absolute reaction rate theory. A set of evolution equations has been developed which can account for the effect of chemical crosslink density on the relaxation rate. The rate equation to describe mechanically coupled chain scission processes has also been proposed. These equations which represent the coupled chemomechanical behaviour of the polymer, are complex and highly nonlinear. In this paper, we try to solve the equations for specific loading conditions such as constant strain (stress relaxation), constant strain rate, stress relaxation with sudden change of crosslink density, etc., to illustrate the ageing behaviour the equation will represent. Finally, the creep behaviour of time-dependent chemically unstable materials is developed. In order to do this, the Gibbs free energy is introduced, in which the state of strain is expressed in terms of stress and temperature.

In order to proceed in an orderly fashion, we shall review briefly in the next section the thermodynamic equations and the internal constitutive equation of ageing materials in the context of deformation kinetics as it was proposed and developed in [1].

2. Thermodynamic equations and constitutive equation of internal variables of ageing materials

The fundamental thermodynamic equations that, in principle, apply irrespective of the constitutive properties of a material are [2, 3]

$$\psi = \psi(\mathbf{C}, T, \mathbf{q}^r) \tag{1}$$

$$\boldsymbol{\tau} = 2(\rho/\rho_0)(\partial\psi/\partial\mathbf{C}) \tag{2}$$

$$\eta = -\partial\psi/\partial T \tag{3}$$

$$(\partial\psi/\partial\mathbf{q}^r)(\dot{\mathbf{q}}^r) \leq 0 \qquad (r \text{ not summed}) \tag{4}$$

where ψ is the Helmoltz free energy function. The last inequality is the Clausius–Duhem inequality, where $\mathbf{C}$ is the right Cauchy–Green deformation tensor, T the temperature, ρ and ρ_0 the current and reference densities, respectively, $\boldsymbol{\tau}$ is the stress defined in the material frame of reference, η is the entropy per unit undeformed volume and the $\mathbf{q}^r$ are the internal variables. The basic idea of using internal variables is that, in order to expand the dimensions of the state space of deformation such that one can define uniquely the Helmholtz free energy, ψ, of a system undergoing an irreversible process, it is necessary to introduce a sufficient number of additional state variables (internal variables) which are considered essential for the description of the internal structures of the material.

0022–2461/85 $03.00 + .12

The above set of equations does not include constitutive equations for the internal variables which are essential to account for internal dissipation. These additional equations referred to as "internal constitutive equations" of chemically stable materials have been derived by Valanis and Lalwani [4] using the concept of the activation energy barrier and deformation kinetics. The resulted equations are given by

$$\dot{q}_\alpha + K_1^\alpha \sinh \left(K_2^\alpha \frac{\partial \psi}{\partial q_\alpha} \right) = 0 \tag{5}$$

where K_1^α and K_2^α are non-negative constants given by the equations

$$K_1^\alpha = \frac{2\lambda^\alpha}{t^\alpha} \exp(-\beta\epsilon_0^\alpha) \sum_{\epsilon_r'^\alpha > 0} \alpha \exp(-\beta\epsilon_i^\alpha) \tag{6}$$

$$K_2^\alpha = C_\alpha \beta \lambda^\alpha \tag{7}$$

where ϵ_0^α is the potential barrier height, t^α the average time taken by a molecule to traverse a distance λ^r across the barrier, $\beta = 1/T$, K the Boltzmann constant and ϵ_i^α activated energy above the potential barrier ϵ_0^∞. Equation 5 is a phenomenological constitutive equation derived from kinetic considerations at the molecular level.

For the ageing materials (i.e. chemicially unstable), we can, in general, extend the constitutive equation by adding the ageing parameters, A_i, in the stress–strain equation, i.e.

$$\boldsymbol{\tau} = 2\frac{\rho}{\rho_0} \frac{\partial \psi(\mathbf{C}, \theta, q^\alpha, A_i)}{\partial \mathbf{C}} \tag{8}$$

and in the internal constitutive equation

$$\dot{q}_\alpha + K_1^\alpha(A_i) \sinh \left[K_2^\alpha(A_i) \frac{\partial \psi}{\partial q_\alpha} \right] = 0 \tag{9}$$

The above set of equations is quite general and, in principle, applies irrespective of the constitutive properties which a material possesses[*]. To describe the rate of ageing, a chemomechanical kinetics equation must be introduced. However, the way of introducing ageing parameters depends on the material at hand. It is reasonable to assume that the ageing effect of network polymer is mainly manifested by the chemical crosslinking or scission of polymer chains, hence the ageing parameter, A_i, will be identified with chemical crosslinking density, ν. In our previous paper, we considered the network polymer undergoing a scission process. In order to describe the kinetic process of molecular motion, a network "skeleton model" was proposed by postulating that a cross-linked polymer consists of a three-dimensional skeleton of chemically bonded chains which is imbedded in a milieu of entangled uncrosslinked free molecules. We further postulated that, due to slow slippage of entanglements along the main crosslinked chain, the entanglements force the skeleton to relax slowly and ponderously. We further consider that crosslinking has primarily two effects. One is to reduce the length of chains between crosslinks and the other is to reduce the number of entanglements, i.e. decreasing the number density or concentration of the molecular liquid or of the free chains, thus accelerating the relaxation processes.

If the process of relaxation is regarded as a process of overcoming energy barriers presented by collision with free chains, then one can reason that the less the concentration of free chains, the less the probability of meeting an energy barrier.

Returning to the question of introducing ageing parameters, let the energy to overcome the resistance of a single free chain to the relaxation process of a crosslinked chain be θ. Thus if m is the average number of free chains in the relaxation path of a crosslinked chain, then the energy required for relaxation is $m\theta$. Let ν_T be the total number of network linkages which include the chemical crosslinks, ν, plus the total number of weak intermolecular force interacting sites, ν_{eN}, which include weak friction points due to entanglements and some causal friction contacts. We consider the number of ν_T to be large and to stay constant throughout deformation. We postulate that a small change of crosslink density will not affect the total number of ν_T, or we may consider that the increase of chemical crosslinks will replace the friction points where the weak intermolecular interacting occurs. Thus we assumed ν_T to be essentially constant in the course of a small change in crosslinking. Hence we assume

$$\nu_{eN} + \nu = \nu_T = \text{constant} \tag{10}$$

It is also reasonable to assume that a linear relationship exists between ν_{eN} and ν. Also if N is the number of free chains then, on purely topological considerations, it is reasonable to expect a linear relationship of the type

$$\nu_{eN} = aN + b \tag{11}$$

where a and b are positive constants.

---

[*] Equations 8 and 9 are shown for the first time and are not included in [1].

Thus, from Equations 10 and 11:

$$N = \frac{\nu_T - b}{a} - \frac{\nu}{a} \tag{12}$$

Since m is proportional to N then the energy, ϵ, required for relaxation per chain is

$$\epsilon = \alpha'\theta\left(\frac{\nu_T - b}{a} - \frac{\nu}{a}\right) \tag{13}$$

where α' is a proportionality constant.

The above expression may be written in the form

$$\epsilon = \bar{\epsilon}_0 - \gamma\nu \tag{14}$$

where $\bar{\epsilon}_0$ is a reference energy and γ is a positive constant.

In relation to the theory of deformation kinetics and as a result of Equation 14, the rate constant, K_1, is given by Equation 15.

$$K_1 = \frac{2\lambda}{\tau} \exp\left[-(\epsilon_0 - \gamma\nu/\kappa T)\right] \sum_r \frac{1}{\alpha} \exp(-\beta\epsilon_i^r). \tag{15}$$

The above equation may be written in the form:

$$K_1 = K_1^0 \exp(\gamma\nu/\kappa T) \tag{16}$$

where K_1^0 is a reference value of K_1, in which the material is chemically stable.

By substituting Equation 16 into Equation 5, we obtain the internal constitutive equation of polymer network

$$\dot{q}_\alpha + \left(\frac{1}{\eta_\alpha^0}\right) \exp(\gamma\nu/\kappa T) \frac{\partial\psi}{\partial q_\alpha} = 0 \tag{17}$$

where

$$K_1^\alpha K_2^\alpha = \frac{1}{\eta_\alpha^0} \exp(\gamma\nu/\kappa T) \tag{18}$$

and now the ageing parameter, $A_i = \nu$, is properly introduced into the evolution equation to describe the chemomechanical behaviour. Finally, we assume that if the scission process is purely chemical and is unaffected by the presence of a stress field, then the rate of change of ν is governed by the classical rate equation:

$$\frac{d\nu}{dt} + \frac{\nu}{g} kT \exp(-\epsilon_0/kT) = 0 \tag{19}$$

where ϵ_0 is the bond energy of a bond in the set of bonds ν, and g is Planck's constant. The bond energy is, essentially, the potential energy barrier to the dissociation process.

It is, however, quite natural to presume that the presence of the stress field will have an effect on the scission process, through a change in the potential energy barrier, ϵ_0.

In keeping with our previous arguments on deformation kinetics, we presume that the change, $\Delta\epsilon_0$, in ϵ_0 is due to the presence of a free energy gradient, $\partial\psi/\partial q_r$, and is in fact a function thereof. For the purposes of obtaining explicit results we assume that the dependence is linear and that

$$\Delta\epsilon_0^r = \sum \left|\frac{\partial\psi}{\partial q_r}\right| \mu_r \tag{20}$$

where μ_r are the non-negative material constants. The mechanically coupled scission process is now given by the relation

$$\frac{d\nu}{dt} + \frac{\nu}{g} kT \exp\left[-\left(\epsilon_0^r - \sum \mu_r \left|\frac{\partial\psi}{\partial q_r}\right|\right)/kT\right] = 0 \tag{21}$$

By assuming an explicit expression for the free energy function, Equations 22 to 24, which represent the coupled chemomechanical behaviour of the network polymer, were obtained [1]:

$$\tau = \sum E_r p_r + k\nu e_{11} \tag{22}$$

$$\dot{p}_r + \frac{E_r}{\eta_r^0} \exp(\gamma\nu/kT)\, p_r = \dot{e}_{11} \tag{23}$$

$$\dot{\nu} + b \exp\left(\sum_{r=1}^{r} \mu_r |p_r|\right) \nu = 0 \tag{24}$$

where

$$p_r = e_{11} - q_r \tag{25}$$

and $b = kT/g \exp[-(\epsilon_0/kT)]$. e_{11} is the strain under simple tension.

An explicit solution of the above set of equations under specific loading conditions will be sought in the next section.

3. Mathematical description of relaxation process of certain loading and environmental conditions for ageing materials

In order to describe the relaxation behaviour above the glassy temperature, the WLF equation is applied by modifying Equation 23 as follows:

$$\dot{p}_r + k_r \exp(h\nu)\, a_T p_r = e_{11} \tag{26}$$

where

$$a_T = \exp\left\{2.3026\,\frac{C_1\,(T-T_s)}{C_2+(T-T_s)}\right\} \qquad (27)$$

and h is now a certain function of the variable (γ/k). The coefficients k_r and h are now independent of temperature. Here we attempt to describe the ageing behaviour coupled with temperature and strain histories, using the above equations:

3.1. Relaxation only (no chain scission)

If we assume there is no chemical scission occurring during relaxation, then only Equations 22 and 26 are needed. Thus the equations become:

$$\tau = \sum_{r=1}^{r} E_r p_r + k\nu e_{11} \qquad (28)$$

$$\dot{p}_r + k_r a_T \exp(k\nu)\,p_r = 0 \qquad (29)$$

where e_{11} is a constant uniaxial strain applied during unit step loading, and ν is constant. At constant temperature, $T = T_0$, we have

$$p_r = p_r^0 \exp\left[-k_r a_{T_0} \exp(h\nu)t\right] \qquad (30)$$

At the initial condition, $q(0^+) = 0$, thus we have $p_r^0 = e_{11}$. Substituting this relation and Equation 29 into Equation 28, we have

$$\tau = e_{11} \sum E_r \exp\left[-k_r t a_T \exp(h\nu)\right] + k\nu e_{11}. \qquad (31)$$

Since the time-dependent relaxation modulus is defined by

$$\Delta E = \frac{\tau - k\nu e_{11}}{e_{11}} \qquad (32)$$

we have:

$$\Delta E = \sum E_r \exp\left[-k_r a_T \exp(h\nu)t\right]$$

$$= \bar{\Delta} E\left[a_T \exp(h\nu)t\right] \qquad (33)$$

The above equation states that the shift factor due to crosslink density is an exponential rather than a power function of ν. This relation has been discussed in [1]; however, here we have modified Equation 23 into Equation 26 to include the temperature dependence through the time-temperature shift factor a_T.

3.2. Chain scission only (no physical relaxation)

Under a unit step loading and no physical relaxation, we have $e_{11} = 0$ and $q_r = 0$ at time $t > 0$. Thus from Equations 25 and 26, we have $p_r = 0$ and $q_r = e_{11}$. Hence Equations 22 and 24 become

$$\tau = k\nu e_{11} \qquad (34)$$

and

$$\dot{\nu} + \nu\frac{\kappa T}{g}\exp\left(-\frac{\epsilon_0}{\kappa T}\right) = 0 \qquad (35)$$

For constant temperature, T_0, we have from Equation 35,

$$\nu = \nu_0 \exp\left[-\left(\frac{\kappa T_0}{g}\right)\exp\left(-\frac{\epsilon_0}{\kappa T_0}\right)t\right] \qquad (36)$$

Thus we have:

$$\frac{\tau(t)}{\tau(0)} = \exp\left[-\left(\frac{\kappa T_0}{g}\right)\exp\left(-\frac{\epsilon_0}{\kappa T_0}\right)t\right] \qquad (37)$$

which agrees with Tobolsky's data [5] on scission process at elevated temperature, where no physical relaxation occurs.

Alternatively, one may also observe from Tobolsky's data (Fig. 1) that the strain effect on the scission process is small for some types of polymeric materials. Thus, it is reasonable to assume that $\mu_r \approx 0$ in Equation 24 for our current analysis. Hence Equation 24 again becomes

$$\dot{\nu} + \nu\frac{\kappa T}{g}\exp\left(-\frac{\epsilon_0}{\kappa T}\right) = 0 \qquad (38)$$

3.3. Simultaneous physical relaxation and chemical ageing

Here we would like to consider the phenomenon such that both physical relaxation and chemical ageing occur simultaneously. First, we consider that this phenomenon occurs at constant temperature, which simplifies the analysis considerably.

3.3.1. Constant temperature

At constant temperature, the solution of Equation 38 is

$$\nu = \nu_0 \exp(-b_0 t) \qquad (39)$$

where

$$b_0 \equiv \frac{\kappa T_0}{g}\exp(-\epsilon_0/\kappa T_0) \qquad (40)$$

which is the scission rate constant at temperature, T_0. If the rate constant b_0 is small, e.g. of the order of $8.0 \times 10^{-4}\ \text{min}^{-1}$ as observed by Tobolsky for natural rubber, expansion of Equation 39 into a power series leads to

$$\nu \simeq \nu_0\,(1 - b_0 t) \qquad (41)$$

It is obvious that time, t, will not be too large to

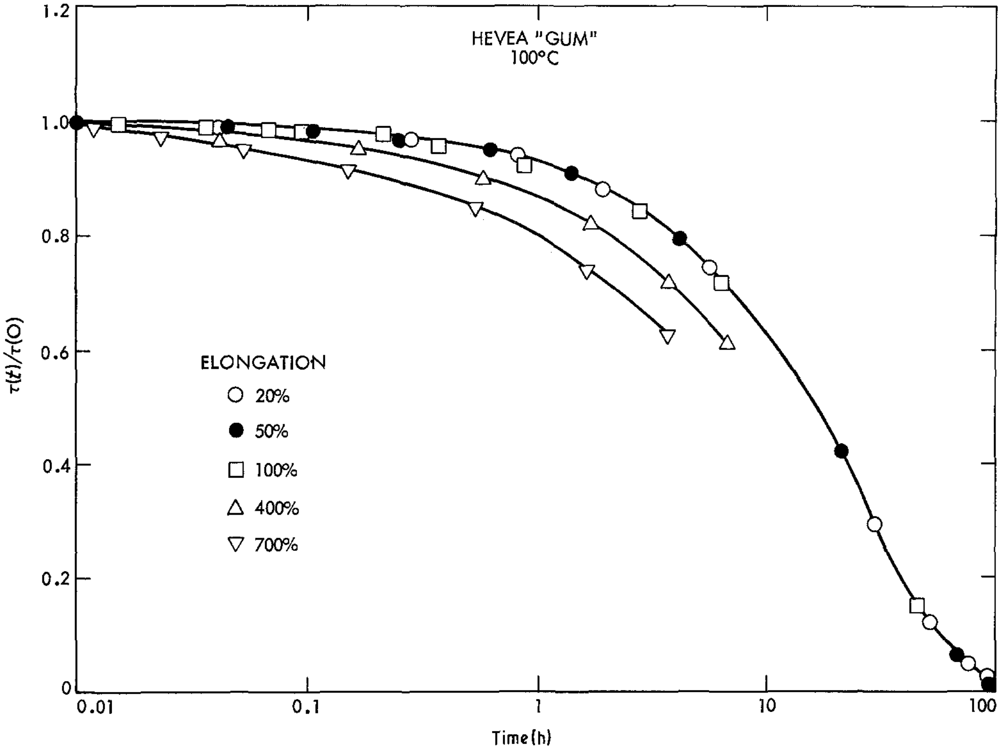

Figure 1 Effect of elongation on chemical stress relaxation of natural rubber at 100° C (after Tobolsky *et al.* [5]).

affect the expansion. Now, substituting Equation 40 into the evolution Equation 26 we have

$$\dot{p}_r + l_r \exp(-h\nu_0 b_0 t)\, p_r = \dot{e}_{11} \qquad (42)$$

where

$$l_r \equiv k_r a_{T_0} \exp(h\nu_0) \qquad (43)$$

The solution of Equation 42 is given by

$$p_r = \exp\left[\frac{l_r}{c}\exp(-ct)\right]\int^t \dot{e}_{11} \times \exp\left[-\frac{l_r}{c}\exp(-c\tau)\right]\mathrm{d}\tau + C_1 \exp\left[\frac{l_r}{c}\exp(-ct)\right] \qquad (44)$$

where $c \equiv h\nu_0 b_0$ and C_1 is the integration constant.

Next we consider three subsets of loading history:

3.3.1.1. Stress relaxation. Under stress relaxation conditions, we have from Equation 44 the solution

$$p_r = e_{11} \exp\left[\frac{l_r}{c}\exp(-ct)\right] \qquad (45)$$

Substituting Equations 45 and 41 into Equation 22, we have

$$\tau = \left[\sum E_r \exp\,[(l_r/c)\,\mathrm{e}^{-ct}] + k\nu_0(1-bt)\right] e_{11}\,. \qquad (46)$$

Using Equation 32, the time dependent relaxation modulus becomes

$$\Delta E = \sum E_r \exp\left[\frac{l_r}{c}\exp(-ct)\right] - \kappa\nu_0\, bt \qquad (47)$$

In the limiting case, where $c \to 0$ ($b_0 \to 0$) such that the scission process is near zero, then we have

$$\lim_{c\to 0}\frac{\exp(-ct)}{c} = -t \qquad (48)$$

hence Equation 47 becomes

$$\Delta E(t) = \sum E_2 \exp(-l_r t) = \Delta E[a_T \exp(h\nu_0)t] \qquad (49)$$

which is the physical relaxation modulus obtained before. It is clear by comparing Equations 47 and 49 that the rate of relaxation is modified by the

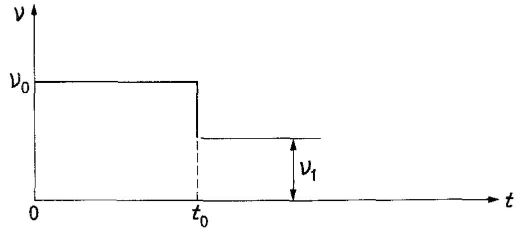

Figure 2 Sudden change of crosslink density.

function $1/c\ e^{-ct}$, and $k\nu_0 bt$ which affects the modulus directly by changing crosslink density.

3.3.1.2. Constant strain rate. In a constant strain rate experiment, we have

$$p_r = \dot{e}_{11} \exp\left[\frac{l_r}{c}\exp(-ct)\right] \times \int_0^t \exp\left[-\frac{l_r}{c}\exp(-ct)\right] \mathrm{d}t \qquad (50)$$

and

$$\tau = \dot{e}_{11} \sum E_2 \exp\left[\frac{l_r}{c}\exp(-ct)\right] \times \int_0^t \exp\left[-\frac{l_r}{c}\exp(-ct)\right] \mathrm{d}t + k\nu_0 \exp(-b_0 t)\, e_{11}(t) \qquad (51)$$

If there is no scission process, then Equation 51 reduces to

$$\tau = \dot{e}_{11} \sum \frac{E_r}{l_r}[1 - \exp(-l_r t)] + k\nu_0 e_{11}(t) \qquad (52)$$

which is again the representation of classical linear viscoelastic behaviour.

3.3.1.3. Stress relaxation with sudden change of ν. During the relaxation process, if the crosslink density suddenly changes as shown in the Fig. 2, then the relaxation will change accordingly. By solving Equation 26 directly, one can predict the relaxation behaviour without recourse to assumptions used by Moacanin *et al.* [6] and Curro and Salazar [7], which are discussed by Huang and Aklonis [8].

For the time interval $0 < t < t_0$, the stress is given by (for constant crosslink density, ν_0)

$$\tau = \overline{\Delta E}(a_T \exp(h\nu_0)t)e_{11} + k\nu_0 e_{11} \qquad (53)$$

For time $t_0 < t$, the crosslink suddenly decreases to ν_1 at $t = t_0$, then the stress is given by

$$\tau = \sum_{r=1}^{r} E_r \exp[-(l_r + l_r')t_0] \exp(-l_r' t)\, e_{11} + k\nu_1 e_{11} \qquad (54)$$

where

$$l_r' = a_{T_0} E_r \exp(h\nu_1) \qquad (55)$$

and

$$l_r = a_{T_0} E_r \exp(h\nu_0) \qquad (56)$$

and the relaxation modulus is given by

$$\Delta E(t > t_0) = \sum E_r \exp[-(l_r + l_r')t_0] \exp(-l_r' t) \qquad (57)$$

3.3.2. With temperature history during ageing

If the temperature history is included, then the set of Equations 26 and 38 becomes very complex. There is no simple analytical solution, although one may solve numerically the set of coupled systems of differential equations. However, the representation of Equations 22, 24 and 26 offers wider flexibility than other approaches [6, 7], since it takes into account explicitly the coupled effects of temperature and strain history, and chain scission of the network on relaxation behaviour.

On comparison with Equation 49, one may observe that the relaxation modulus is modified by the terms $\exp[-(l_r + l_r')t_0]$, and it seems that Equation 57 cannot be simply related to Equation 49.

4. Gibbs free energy formulation – stress formulation

In the previous formulation to describe the relaxation behaviour, the Helmholtz free energy was employed, where the independent variables are the right Cauchy–Green strain tensor, C_{ij}, the absolute temperature T and r internal variables q_r. In order to describe the creep behaviour, the Gibbs free energy, Φ, is now introduced which leads to constitutive equations expressed as functions of stress and temperature. In the Gibbs free energy formulation, the Piola stress tensor, τ_{ij}, the absolute temperature T and q_r become the independent variables.

First, we introduce the Gibbs free energy, Φ, by the relation

$$\Phi = \psi - \tfrac{1}{2}\tau_{ij}C_{ij} \qquad (58)$$

As a result of Equation 58, one has

$$d\Phi = \frac{\partial\psi}{\partial C_{ij}}dC_{ij} + \frac{\partial\psi}{\partial q_\alpha}dq_\alpha + \frac{\partial\psi}{\partial T}dT - \tfrac{1}{2}\tau_{ij}dC_{ij} - \tfrac{1}{2}C_{ij}d\tau_{ij} \qquad (59)$$

Recall that

$$\tau_{ij} = \tfrac{1}{2}\,\frac{\partial\psi}{\partial C_{ij}} \text{ and } \eta = -\frac{\partial\psi}{\partial T} \qquad (60)$$

Thus, one has

$$d\Phi = \frac{\partial\psi}{\partial q_\alpha}dq_\alpha + \frac{\partial\psi}{\partial T}dT - \tfrac{1}{2}C_{ij}d\tau_{ij} \qquad (61)$$

Since

$$d\Phi = \frac{\partial\Phi}{\partial\tau_{ij}}\,d\tau_{ij} + \frac{\partial\Phi}{\partial T}\,dT + \frac{\partial\Phi}{\partial q_\alpha}\,dq_\alpha \qquad (62)$$

by comparing Equation 61 and 62, we have

$$\tfrac{1}{2}C_{ij} = \frac{\partial\Phi}{\partial\tau_{ij}} \qquad (63)$$

$$\frac{\partial\Phi}{\partial q_\alpha} = \frac{\partial\psi}{\partial q_\alpha} \qquad (64)$$

and

$$\frac{\partial\Phi}{\partial T} = \frac{\partial\psi}{\partial T} = -\eta \qquad (65)$$

It is interesting to note that Equation 64 shows that the internal force is derivable from the potential energy surface expressed either by the Helmholtz free energy or the Gibbs free energy.

In the case of uniaxial loading with small strain, e_{11}, Equation 63 becomes

$$e_{11} = -\frac{\partial\Phi}{\partial\tau} \qquad (66)$$

Let us now expand the free energy with respect to stress τ and q_α, and assume that they are so small that terms higher than second-order in these terms can be neglected, i.e.

$$\Phi = -\tfrac{1}{2}J_0\tau^2 - \sum D_\alpha\tau q_\alpha + \sum\frac{F_\alpha}{2}q_\alpha^2 \qquad (67)$$

where the coefficient of the linear term must be zero, and J_0, D_α and F_α are constants.

However, it is of interest to consider a mechanical model to compare Equation 67, e.g. a three-element model with a Maxwell element [2, 9] (Fig. 3). From Fig. 3, one obtains the expression of Helmholtz free energy function as

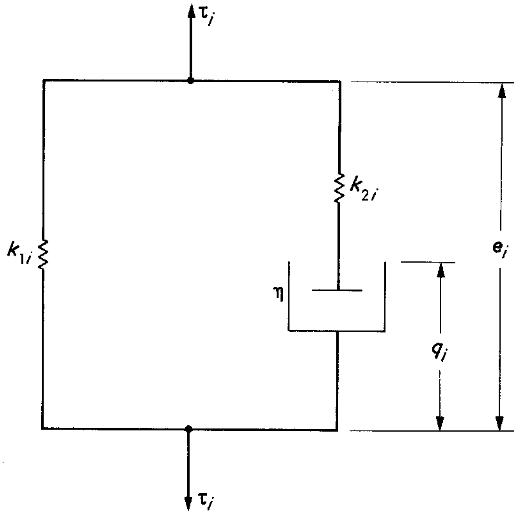

Figure 3 Three-element model with a Maxwell element.

$$\psi_i = \tfrac{1}{2}k_{1i}e_i^2 + \tfrac{1}{2}k_{2i}(e_i - q_i)^2 \qquad (68)$$

and†

$$\tau = \frac{\partial\psi_i}{\partial e_i} = k_{1i}e_i + k_{2i}(e_i - q_i) \qquad (69)$$

Since

$$\Phi_i = \psi_i - \tau e_i \qquad (70)$$

then, using Equations 68 and 69, one obtains Φ_i expressed in terms of q_i and τ, i.e.

$$\Phi_i = -\frac{\tau^2}{2(k_{1i}+k_{2i})} - \frac{k_{2i}}{k_{1i}+k_{2i}}\tau q_i + \frac{k_{1i}k_{2i}}{2(k_{1i}+k_{2i})}q_i^2 \qquad (71)$$

If we consider the three-element model in a series configuration, then we have

$$\Phi = \sum\Phi_i = \sum_{i=1}^{n} -\frac{\tau^2}{2(k_{1i}+k_{2i})} - \sum_{i=1}^{n}\frac{k_{1i}}{k_{1i}+k_{2i}}\tau q_i + \sum_{i=1}^{n}\frac{k_{1i}k_{2i}}{2(k_{1i}+k_{2i})}q_i^2 \qquad (72)$$

By comparing Equation 72 with Equation 67, we obtain

$$J_0 = \sum\frac{1}{k_{1i}+k_{2i}} \qquad (73)$$

$$D_i = \sum\frac{k_{2i}}{k_{1i}+k_{2i}} \qquad (74)$$

---

† Here τ can be calculated directly also from the model: Since $\tau_{1i} = k_{1i}e_i$ and $\tau_{2i} = k_{2i}(e_i - q_i)$ and since $\tau = \tau_{1i} + \tau_{2i}$ then $\tau = k_{1i}e_i + k_{2i}(e_i - q_i)$, as in Equation 69.

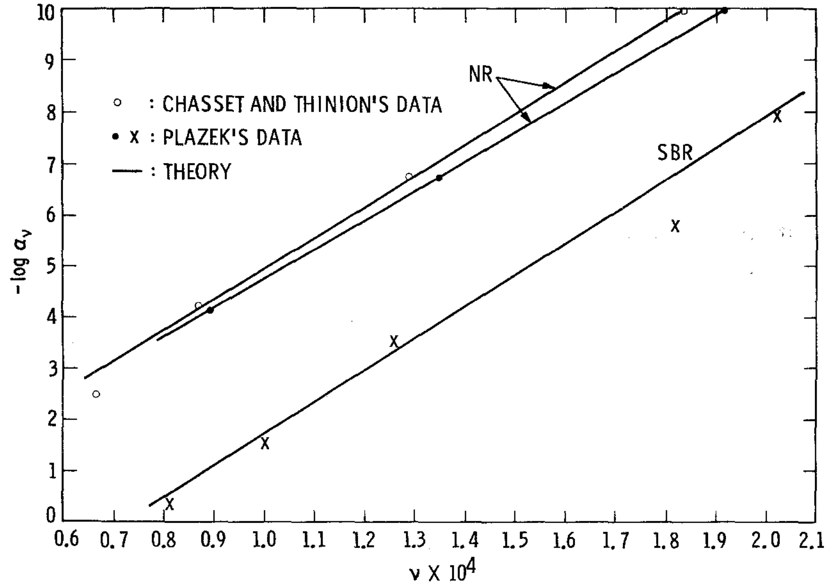

Figure 4 Theoretical prediction of the shift function $A_\nu = \exp(h\nu)$.

and

$$F_i = \sum \frac{k_{1i}k_{2i}}{k_{1i} + k_{2i}} \tag{75}$$

To our knowledge, Equations 71 and 72 show for the first time the relations between mechanical models and internal variables in the creep expressions, using the three-element model with a Maxwell element.[‡] It is also noted that the constants J_0, D_i and F_i are non-negative.

Substituting Equation 67 into Equation 66, one obtains

$$e_{11} = J_0\tau + \sum D_\alpha q_\alpha \tag{76}$$

From Equations 64 and 17, we have

$$\dot{q}_\alpha + k_r \exp(h\nu)\, a_T \frac{\partial\Phi}{\partial q_\alpha} = 0 \tag{77}$$

thus, with Equation 67, we have the evolution equation:

$$\dot{q}_\alpha + k_\alpha \exp(h\nu)\, a_T (-D_\alpha\tau + F_\alpha q_\alpha) = 0 \tag{78}$$

Now the mechanically coupled scission equation can be written as

$$\frac{\mathrm{d}\nu}{\mathrm{d}t} + \frac{\nu}{g}\kappa T \exp\left[-\left(\epsilon_0^r - \sum \mu_r \left|\frac{\partial\Phi}{\partial q_r}\right|\right)\Big/\kappa T\right] = 0 \tag{79}$$

Equations 76, 78 and 79 represent the chemomechanical behaviour of ageing materials undergoing creep.

It is of interest to illustrate the effect of ν on creep behaviour for a non-ageing network polymer. Under constant stress and constant temperature T_0, i.e. $\tau = \tau_0$ and $T = T_0$ we have from Equation 78

$$q_\alpha = m_\alpha [1 - \exp(-n_\alpha t \mathrm{e}^{h\nu} a_T)]\tau_0 \tag{80}$$

where $m_\alpha \equiv D_\alpha/F_\alpha$, $n_\alpha \equiv K_\alpha F_\alpha$. Substituting Equation 80 into Equation 76, one has

$$e_{11} = J_0\tau_0 + \sum l_r [1 - \exp(-n_\alpha t \mathrm{e}^{h\nu} a_T)]\tau_0 \tag{81}$$

Thus

$$\Delta J = \frac{e_{11} - J_0\tau_0}{\tau_0} = \sum l_r [1 - \exp(-n_\alpha t \mathrm{e}^{h\nu} a_T)]$$
$$= \overline{\Delta J}\,[t a_T \exp(h\nu)] \tag{82}$$

Therefore, the shift factor of time for creep compliance is given by $\mathrm{e}^{h\nu}$, and this form is compared with Plazek's creep data [11] in Fig. 4. Agreement of the shift factor with the exponential form is excellent. Thus it is reasonable to believe that Equations 76, 77 and 79 can represent the coupled chemomechanical behaviour of the

---

[‡] Schapery [10] used a Voigt element in series for his mechanical model. In this model, we found that the coefficients in Equation 67 cannot be related explicitly.

polymer undergoing simple creep, in which the effect of scission of chain on the rate of creep is expressed explicitly.

Acknowledgement

This paper represents one phase of research performed by the Jet Propulsion Laboratory, California Institute of Technology, sponsored by the National Aeronautics and Space Administration, Contract NAS7-918.

References

1. K. C. VALANIS and S. T. J. PENG, *Polymer* **24** (1983) 1551.
2. K. C. VALANIS, Iowa State University Report 52 (1967).
3. B. D. COLEMAN and M. E. CURTIN, *J. Chem. Phys.* **47** (1967) 597.
4. K. C. VALANIS and S. LALWANI, *ibid.* **67** (1977) 3980.
5. A. V. TOBOLSKY, I. B. PRETTYMAN and J. H. DILLON, "Properties and Structure of Polymer" (Wiley, New York, 1960).
6. J. MOACANIN, J. U. AKLONIS and R. F. LANDEL, *J. Chem. Phys.* **64** (1976) 430.
7. J. G. CURRO and E. A. SALAZAR. *J. Appl. Polymer Sci.* **19** (1975) 2571.
8. W. N. HUANG and J. J. AKLONIS, *J. Macromol. Sci. Phys.* **15** (1978) 45.
9. H. LEADERMAN, Viscoelasticity Phenomena in Amorphous High Polymeric Systems, in "Rheology," Vol. 2, edited by F. R. Eirich (Academic Press, New York, 1958) Ch. 1.
10. R. A. SCHAPERY, "Further Development of a Thermodynamic Constitutive Theory: Stress Formulation", Purdue University Report AA & ES 69-2 (1969).
11. D. PLAZEK, *J. Polymer Sci. A-2* **4** (1966) 745.

Received 8 February
and accepted 6 April 1984