Deformation kinetics of ageing materials*

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(*Received* 12 *October* 1982)

A constitutive equation of time-dependent, chemically stable materials, which stems from the basic ideas of the irreversible thermodynamics of an internal variable and Eyring's absolute reaction rate theory, has been extended to chemically unstable materials. This formulation is quite general and, in principle, can be applied to many types of materials. In this paper, the ageing behaviour of time-dependent network polymers undergoing chain scission is considered. In the network scission process, we postulate that the energy barrier is affected by a changing of the chemical crosslink density. An explicit equation to account for the energy barrier change, which influences the relaxation process, is formulated. For the purpose of illustration, the effect of different chemical crosslink density, ν, on the relaxation rate has been considered, from which the following theoretical expression of relaxation modulus $\Delta E(t)$ is obtained:

$$\Delta E = \Delta E^{\circ}[t \exp(\gamma\nu/kT)]$$

It can be seen that a change in ν leads to an effective change in the time scale, usually denoted by a_x. Here the analytical expression $a_x = \exp(\gamma\nu/kT)$ correlates quite well with the experimental data.

Keywords Ageing; relaxation function; crosslink density; entanglements; bond scission; energy barrier

INTRODUCTION

Previously[1] we used the formalism of irreversible thermodynamics of internal variables as a framework for the development of constitutive equations for 'chemically stable materials'. Such materials can be defined in a physical context by saying that their properties (physical, mechanical or thermal) remain unchanged with the passage of time when they are in an unstressed state. Equivalently, they may be defined in a mathematical context by a statement to the effect that their constitutive equations remain invariant with a time translation. Equally well one may define a chemically stable material in an experimental context by stipulating that the time of origin of an experiment has no effect on the material response observed.

In this paper we shall deal with the development of constitutive equations for materials that are *not* chemically stable. This we shall do by recourse to the theories of thermodynamics of internal variables and absolute rate processes as they were developed by the first author and his co-workers.

The original theory of absolute reaction rates was first proposed by Eyring[2]. This theory has more recently been referred to as 'deformation kinetics'. It is this term that we shall be using in the remainder of this paper.

In order to proceed in an orderly fashion we shall review briefly the theory of internal variables in the context of deformation kinetics of stable materials, as it was proposed and developed in ref. 3.

The basic idea behind the theory of internal variables is that, in order to define uniquely the Helmholtz free energy ψ of a 'system' undergoing an irreversible process, one has to expand the dimensions of the state space of deformation and temperature (state variables commonly employed in classical thermodynamics to study elastic materials) by introducing a sufficient number of additional state variables which are considered essential for the description of the internal structure of the material in question. The n thermodynamic variables $\utilde{q}^r$ are the additional variables necessary to define the thermodynamic state of a material system.† The number n of these variables is related to the material structure as well as to the degree of accuracy with which one wishes to represent the material response.

The fundamental thermodynamic equations that, in principle, apply irrespective of the constitutive properties of a material are, in the notation of ref. 3:

$$\psi = \psi(\utilde{C}, \theta, \utilde{q}^r) \tag{1}$$

$$\utilde{t} = 2(\rho/\rho_0)(\partial\psi/\partial\utilde{C}) \tag{2}$$

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

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

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* 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 NAS7-100

† A tilde under any symbol will denote a second-order tensor; a double tilde a fourth-order tensor

0032-3861/83/121551-07$03.00

The last inequality is the Clausius–Duhem inequality, whereas $\underset{\sim}{C}$ is the right Cauchy–Green deformation tensor, θ the temperature, ρ and ρ_0 the current and reference densities, respectively $\underset{\sim}{\tau}$ is the stress defined in the material frame of reference, η is the entropy per unit undeformed volume, and the dot over $\underset{\sim}{q}^r$ denotes differentiation with respect to time t.

The above set of equations does not include constitutive equations for the internal variables. These *additional* equations, referred to as 'internal constitutive equations', determine, in fact, the mechanical response of the particular material. In general, these are of the form

$$\mathrm{d}\underset{\sim}{q}^r/\mathrm{d}t=\underset{\sim}{f}^r(\underset{\sim}{C},\underset{\sim}{q}^k,\theta) \qquad (5)$$

for all r, where $\underset{\sim}{f}^r$ are material functions. Valanis[1] used the Clausius–Duhem inequality as a starting point to obtain as a first approximation a linear 'internal constitutive equation' relating the internal forces $\partial\psi/\partial\underset{\sim}{q}^r$ to the rate of change of the internal variables, henceforth called internal velocities or fluxes, i.e.

$$\frac{\partial\psi}{\partial\underset{\sim}{q}^r}+\underset{\sim}{b}^r\cdot\frac{\mathrm{d}\underset{\sim}{q}^r}{\mathrm{d}t}=0 \qquad (r\text{ not summed}) \qquad (6)$$

where $\underset{\sim}{b}^r$ are positive semidefinite viscosity tensors of fourth order.

This equation is likely to be valid in situations where the atomic or molecular motions are 'extremely slow and/or small', as a consequence of the approximation used in its derivation. This linear internal constitutive equation has been applied with success to describe the thermomechanical response of materials[4]. In cases where the relation between the internal forces $\partial\psi/\partial\underset{\sim}{q}^r$ and the time rate of change of the internal variables $\mathrm{d}\underset{\sim}{q}^r/\mathrm{d}t$ is not linear, i.e. for 'finite' atomic motions, one is at a loss to determine the precise nature of the non-linear relation. Such a relation was established in section III of ref. 3 using statistical mechanics and the concept of potential energy barriers. The linear internal constitutive equation (6) was then shown to be a special case of this non-linear equation in the case of 'extremely slow and/or small motions'. In the process of establishing the relationship between internal forces and fluxes, Valanis and Lalwani proposed for the first time a precise physical interpretation of the internal variables which had, so far, played the role of physically nebulous but essential mathematical and thermodynamic variables needed to define the thermodynamic state uniquely.

An *internal variable* in the theory of ref. 3 represents the *average displacement of a group of atoms whose motion is impeded by a potential energy barrier of specific magnitude.* The response of a group of atoms to an externally applied force field then constitutes the mechanism which operates on the atomic level and thereby contributes to the gross process.

Another important element of the theory we feel lay in identifying the microforce, on a group of atoms, which arises as a result of an externally applied stress field. Valanis and Lalwani identified the microforce as the free energy gradient $\partial\psi/\partial\underset{\sim}{q}^r$ that causes the flux $\mathrm{d}\underset{\sim}{q}^r/\mathrm{d}t$. Hitherto, it had been difficult to establish a relationship between the external stress and the microforce encountered in the Eyring theory and resort to mechanical models has been necessary in order to establish such relationships. In contrast, this microforce was given an identity in section III of ref. 3 and its relationship with the external stress was established.

The same ideas apply almost without change to the deformation and ageing of polymers, the subject we deal with in this paper. An internal variable in the present case represents the average displacement of a group of molecules whose motion is impeded by a potential energy barrier of a specific height. Similarly, the microforce is the free energy gradient $\partial\psi/\partial\underset{\sim}{q}^r$ which causes the flux $\mathrm{d}\underset{\sim}{q}^r/\mathrm{d}t$.

THEORY OF ABSOLUTE RATE PROCESSES

The theory of absolute reaction rates stemmed from the proposal made by S. Arrhenius, concerning the influence of temperature on reaction rates, which resulted in the well known 'Arrhenius law'. Arrhenius introduced in this law the concept of activated molecules and the equilibrium of these molecules with the reactant molecules.

The theory of rate processes as proposed by Eyring[2] is based on the idea that any rate process is characterized by an initial configuration which passes by means of a continuous change of the coordinates into the final configuration (via an intermediate configuration) called the activated state of the system. The activated state is situated at the highest point of the most favourable part on the potential energy surface.

The specific rate constant κ of the rate process is expressed as follows:

$$\kappa=\frac{kT}{h}\,\frac{F_T^T}{F_A F_B\ldots}\exp(-\varepsilon_0/kT) \qquad (7)$$

where k is the Boltzmann constant, T the absolute temperature, h is Planck's constant, F_T^T is the partition function of the activated complexes, F_A, F_B are the partition functions of the initial reactants, and ε_0 the activation energy.

In the case of inelastic deformation of solids, κ represents the frequency of crossing of an energy barrier by a group of atoms. This information leads to the derivation of an expression for the velocity of atoms. In addition, if the effect of external stress on the potential barriers were known, a relationship between this effect and the velocity of atoms could be established. This would, in fact, be the 'internal constitutive equation'. In section III of ref. 3, such a relationship was determined for the first time. In this paper we shall apply these ideas to the deformation and ageing of polymers.

INTERNAL CONSTITUTIVE EQUATIONS AND ENERGY BARRIERS

As noted earlier, in cases where the relation between the internal forces $\partial\psi/\partial\underset{\sim}{q}^r$ and the time rates of change of the internal variables $\underset{\sim}{q}^r$ is not linear, the precise nature of the non-linear relation is not known. In ref. 3 Valanis and Lalwani established such a relation between $\partial\psi/\partial\underset{\sim}{q}^r$ and $\dot{\underset{\sim}{q}}^r$ in one dimension for what is believed to be the first time. This they did by assuming that the system at the atomic level is in an equilibrium initial configuration. In addition, it was assumed that the temperature is sufficiently high for Boltzmann statistics to be applicable. In this section these ideas are applied to crosslinked polymers, with specific reference to one dimension.

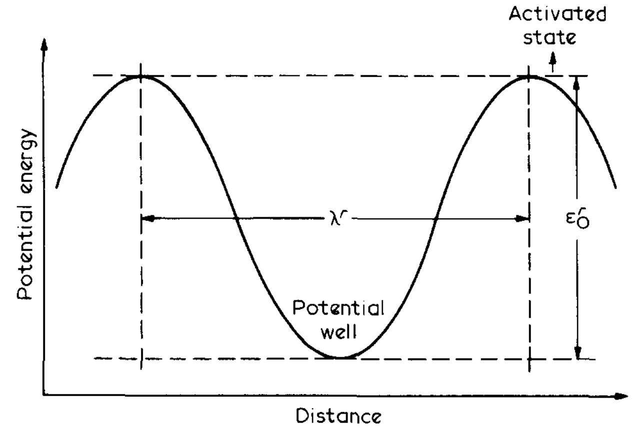

Figure 1 **Symmetric potential energy barriers under no external stress**

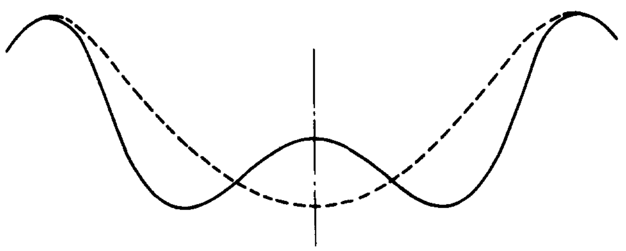

Figure 2 **Symmetric multiple barrier and equivalent single symmetric barrier**

A molecule in an environment of a disordered molecular structure faces potential barriers of different shapes and heights. The height of an energy barrier appropriate to a certain molecule is determined to a good approximation by the immediate environment of that molecule. A molecule has to acquire sufficient energy to surpass such a barrier in its path. When in equilibrium, molecules have a tendency to occupy positions of lowest potential energy as these are the most stable. A large majority of molecules would thus be expected to be found oscillating in wells formed by energy barriers.

It is stipulated that the probability of occurrence of a particular equilibrium configuration of a system is given by the Boltzmann distribution law. Accordingly, the probability p_i of finding a molecule in the energy state ε_i is given by[3]:

$$p_i=\alpha\exp(-\beta\varepsilon_i) \tag{8}$$

where

$$\alpha=1\Big/\sum_i\exp(-\beta\varepsilon_i) \tag{9a}$$

$$\beta=1/kT \tag{9b}$$

For the purpose of deriving appropriate forms of constitutive equations, symmetric barriers will be considered, shown typically in *Figure 1*. It is possible that, in the course of a mechanical test, potential energy barriers exist which are asymmetric. To maintain global equilibrium in the unstressed state, however, it is conjectured that compensating asymmetric barriers exist which result in an overall barrier symmetry. Such an arrangement resulting in a symmetric multiple barrier is shown typically in *Figure 2*, by an unbroken line. Also shown in *Figure 2* is an approximate 'equivalent' single symmetric barrier representation of the multiple barrier configuration.

Such equivalence may be acceptable at higher temperatures; however, 'local asymmetries' may be essential in describing the details of the mechanical response at lower temperatures.

Consider a system of molecules N^r in equilibrium, facing symmetric potential barriers to their motion of height ε_0^r. As these molecules would most probably occupy positions in the wells, one such well is considered, shown in *Figure 1*.

The probability p_0^r that a molecule is in an energy state which is greater than or equal to ε_0^r is:

$$p_0^r=\sum_{\varepsilon_i^r>\varepsilon_0^r}\alpha\exp(-\beta\varepsilon_i^r) \tag{10}$$

States ε_i^r such that $\varepsilon_i^r>\varepsilon_0^r$ we call *activated states*, thus *differing from Eyring*. The number of molecules in an activated state is equal to $N^r p_0^r$, thus:

$$N^r p_0^r=N^r\exp(-\beta\varepsilon_0^r)\sum_{\phi_i'^r>0}\alpha\exp(-\beta\varepsilon_i'^r) \tag{11}$$

where $\varepsilon_i^r=\varepsilon_i^r-\varepsilon_0^r$.

As the barriers are symmetric, the probability of a molecule moving either backwards or forwards with respect to the barrier ε_0^r is the same. The net motion (average velocity) of the molecules N^r is therefore equal to zero. When a stress field at the microscopic level is applied, the resulting gross net motion must imply a redistribution of heights of energy barriers, so that local equilibrium is disturbed leading to average global motion.

The fundamental hypothesis in this paper is that *the molecular level and*, as a result of the application of a stress field, *the potential energy surface in the vicinity of the group of molecules associated with the internal variable q^r suffers a local tilt which is assumed to be linearly proportional to the free energy gradient $\partial\psi/\partial q^r$*. This hypothesis is central in our derivation and should hold if perturbations from the equilibrium configuration are 'sufficiently small'.

This local tilt causes a decrease in the height of the potential energy barriers which oppose motion in the specified direction and a corresponding equal increase in the height of barriers impeding motion in the opposite direction (see *Figure 3*).

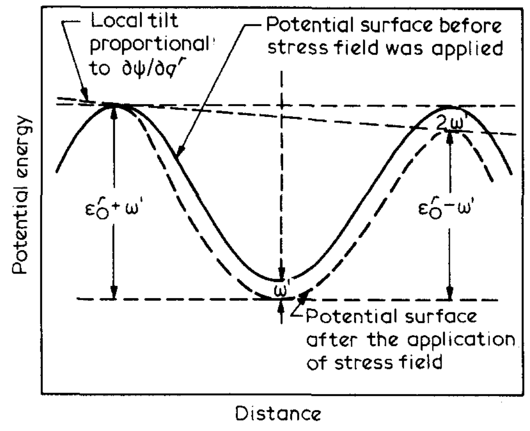

Figure 3 **Potential energy barriers under externally applied stress field**

Let this change in the height of the barriers ε_0^r be denoted by ω^r. The number of molecules with energies greater than $(\varepsilon_0^r - \omega^r)$ is:

$$A^r = N^r \exp[-\beta(\varepsilon_0^r - \omega^r)] \sum_{\varepsilon_i'^r > 0} \alpha \exp(-\beta\varepsilon_i'^r) \quad (12)$$

and the number of molecules with energies greater than $(\varepsilon_0^r + \omega^r)$ is:

$$B^r = N^r \exp[-\beta(\varepsilon_0^r + \omega^r)] \sum_{\varepsilon_i'^r > 0} \alpha \exp(-\beta\varepsilon_i'^r) \quad (13)$$

The net number of molecules that partake in the forward motion is then the number whose energies are greater than $(\varepsilon_0^r - \omega^r)$ but less than $(\varepsilon^r + \omega^r)$, i.e. $A^r - B^r$. This number is given by:

$$A^r - B^r = 2N^r \exp(-\beta\varepsilon_0^r) \sinh(\beta\omega') \sum \alpha \exp(-\beta\varepsilon_i'^r) \quad (14)$$

With reference to *Figure 1*, if τ^r is the average time taken by a molecule to traverse a distance λ^r across a barrier, then the net average velocity $\dot{q}^r$ of molecules in the conventional forward direction is:

$$\dot{q}^r = (\lambda^r/\tau^r)(A^r - B^r)/N^r \quad (15)$$

Here q^r represents the net average displacement of molecules across a potential barrier.

The hypothesis that the local tilt is linearly proportional to the free energy gradient $\partial\psi/\partial q^r$ leads immediately to the equation:

$$\omega^r = -C_r(\partial\psi/\partial q^r)\lambda^r \quad (16)$$

where C_r is the proportionality constant.

Thus it follows from equations (14), (15) and (16) that:

$$\dot{q}^r + K_1^r \sinh\left(K_2^r \frac{\partial\psi}{\partial q^r}\right) = 0 \quad (17)$$

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

$$K_1^r = \frac{2\lambda^r}{\tau^r} \exp(-\beta\varepsilon_0^r) \sum_{\varepsilon_i'^r > 0} \alpha \exp(-\beta\varepsilon_i'^r) \quad (18a)$$

$$K_2^r = C_r\beta\lambda^r \quad (18b)$$

Equation (17) is of fundamental importance in that it is a phenomenological constitutive equation derived from kinetic considerations at the molecular level. Equation (17) was first derived for metals in ref. 3.

Special case of equation (17)

We notice from equations (18a) and (18b) that, if at high temperatures, K_2^r decreases while K_1^r increases, a linear relationship between q^r and $\partial\psi/\partial q^r$ is obtained as a first approximation. If the above assumptions are true, then equation (17) would reduce to the form:

$$\dot{q}^r = -K_1^r K_2^r \partial\psi/\partial q^r \quad (19)$$

Physically speaking, at high temperatures, molecules have enough thermal energy to equilibrate themselves by occupying more stable positions of lowest potential energy. Hence equation (19) should be an appropriate relationship when studying quasistatic processes (processes not far removed from equilibrium). This argument is further supported by the fact that (19) is a special case of (17) in the event of extremely slow net motions $\dot{q}^r$, away from the equilibrium configuration where $\dot{q}^r = 0$. Equation (19) describes very well the mechanical response of linear viscoelastic materials where K_1^r and K_2^r are material constants.

MECHANICAL RESPONSE IN THE PRESENCE OF BOND SCISSION

For the purpose of introducing this section on the mechanical response in the presence of bond scission we shall discuss some general features of relaxation of crosslinked polymers that are consistent with a model which we shall call the 'skeleton model'. In effect a crosslinked polymer consists of a three-dimensional skeleton of chemically bonded chains which is embedded in a milieu of entangled randomly oriented uncrosslinked free molecules, which we shall call the 'molecular liquid'. During the course of relaxation there are two essentially distinct processes that take place simultaneously. The first process is the relaxation of the free molecules themselves; the second is the relaxation of the skeleton. The first is a more rapid process, the skeleton being more ponderous and unwieldy. In reality the first process could be substantially over before the second has time to develop to any significant degree. This is strongly indicated by the intermediate plateau which appears when $E(t)$ is plotted *versus* $\log t$, as shown schematically in *Figure 4*. (The amount and rate of relaxation of skeleton shown in *Figures 4* and *5* are exaggerated. It is important to note that the relaxation processes of crosslinked polymer at this range is very slow and the change of modulus is small compared with whole spectrum of relaxation.)

When the crosslinking density ν is increased, E_R^s will increase and so will E_0^s while E_0 will remain essentially unchanged. The fact that the relaxation of the skeleton is impeded by the molecular liquid implies that the denser the molecular liquid, the slower the relaxation of the skeleton will be, and *vice versa*. As crosslinking increases, the molecular liquid becomes less dense since molecules are subtracted from it and are added to the skeleton. Therefore crosslinking should from some point on begin to increase the rate of relaxation of the liquid as well as that of the skeleton. These statements are summarized in

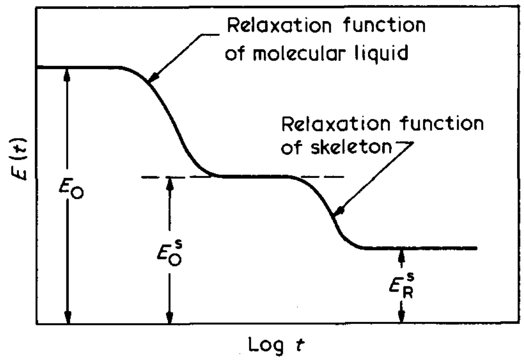

Figure 4 Typical relaxation function of a crosslinked polymer

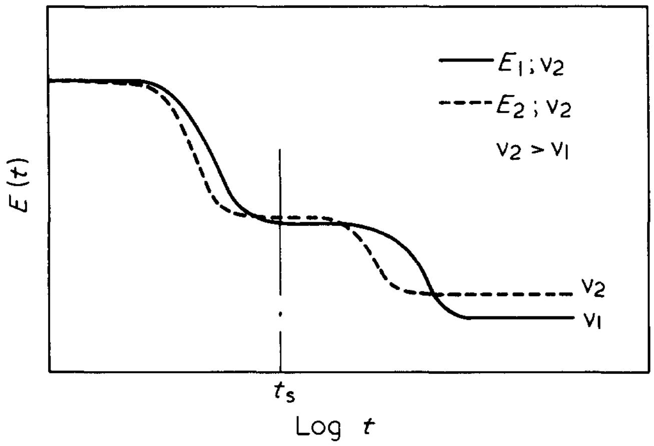

Figure 5 Effect of crosslink density on relaxation function

Figure 5 in terms of two relaxation functions $E_1(t)$ and $E_2(t)$ corresponding to two values ν_1 and ν_2 of ν where $\nu_1 < \nu_2$.

The behaviour illustrated in *Figure 5* is consistent with observation.

In what follows we shall limit ourselves to the relaxation of the skeleton, i.e. we shall examine the relaxation function for $t > t_s$ where the significance of t_s is shown in *Figure 5*..

For the purposes of formulation of the problem we begin with the following equation:

$$\psi = \sum_r \psi_r(\varepsilon - q_r) \qquad (20)$$

which ascribes to each internal atomic or molecular conformation associated with q_r, a free energy ψ_r, and ε is the strain inside the material imposed by stress field. The same equation also implies that the conformational free energies are additive. We now indicate explicitly that ψ_r is a function of the crosslink density ν:

$$\psi_r = \psi_r(\varepsilon - q_r; \nu) \qquad (21)$$

Thus, as before, the total free energy ψ is given:

$$\psi = \sum_r \psi_r(\varepsilon - q_r; \nu) \qquad (22)$$

In a conceptual sense ν may also be regarded as an internal variable of a nature which, however, is decidedly different from that of q_r. This being the case, the stress is obtained from (2), i.e.

$$\tau = \left.\frac{\partial \psi}{\partial \varepsilon}\right|_{q_r, \nu} \qquad (23)$$

The equations of evolution of the internal variables q_r have already been determined and are given by (17), i.e.

$$\dot{q}_r + K_1^r \sinh\left(K_2^r \frac{\partial \psi}{\partial q_r}\right) = 0 \qquad (24)$$

We note that ψ now depends on ν and that the rate of change of q_r now depends implicitly on ν also.

It remains to determine the rate of change of the number of crosslinks ν as a result of scission. 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:

$$\frac{d\nu}{dt} + \frac{\nu}{h} kT^{-\varepsilon_0/kT} = 0 \qquad (25)$$

where ε_0 is the bond energy of a bond in the set of bonds ν. 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 $\Delta\varepsilon_0$ in ε_0 is due to the presence of the free energy gradient $\partial\psi/\partial q_r$ and is in fact a function thereof. Ostensibly, for the purposes of obtaining explicit results we assume that the dependence is linear and that:

$$\Delta\varepsilon_0^r = \sum \left|\frac{\partial \psi}{\partial q_r}\right| \mu_r \qquad (26)$$

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

$$\frac{d\nu}{dt} + \frac{\nu}{h} kT \exp\left[-\left(\varepsilon_0^r - \sum \mu_r \left|\frac{\partial \psi}{\partial q_r}\right|\right) \Big/ kT\right] = 0 \qquad (27)$$

Equations (21)–(27) represent the coupled chemomechanical behaviour of the polymer. The vertical bars denote the absolute value of $\partial\psi/\partial q_r$. These are necessary to ensure that the *sign* of the internal force has no effect on the rate of change of the crosslink density which is a scalar.

APPLICATIONS

For the purposes of illustration we limit ourselves initially to one internal variable and let ψ be of quadratic form. In this case:

$$\psi = \tfrac{1}{2}E_1(\varepsilon - q)^2 + \tfrac{1}{2}K\nu\varepsilon^2 \qquad (28)$$

where K is a constant and E_1 may depend on ν. This simple form of ψ is indeed suitable for application to the long-term relaxation of the skeleton when the conformations with the shorter relaxation times have relaxed and only one remaining configuration plays a role of importance in the relaxation process. We also use the asymptotically linear form of equation (24) and set $(K_1K_2)^{-1} = \eta$. With regard to equation (25) we also set:

$$\frac{kT}{h}\exp(-\varepsilon_0/KT) = b \qquad (29)$$

Then equations (23), (24) and (27) become:

$$\tau = E_1(\varepsilon - q) + K\nu\varepsilon \qquad (30)$$

$$\eta\dot{q} + E_1(q - \varepsilon) = 0 \qquad (31)$$

$$\dot{\nu} + b\exp(\mu|\varepsilon - q|)\nu = 0 \qquad (32)$$

If we now set

$$\varepsilon - q = p \qquad (33)$$

then (30)–(32) become:

$$\tau = E_1 p + K\nu\varepsilon \tag{34}$$

$$\dot{p} + \frac{E_1}{\eta} p = \dot{\varepsilon} \tag{35}$$

$$\dot{\nu} + b\exp(\mu|p|)\nu = 0 \tag{36}$$

Equations (34)–(36) represent the chemomechanical behaviour of a thermodynamic system with one internal variable. The presence of the second term on the right-hand side of (34) ensures the existence of an equilibrium elastic response of the skeleton with an equilibrium modulus ($K\nu$) which is evidently proportional to the crosslink density ν.

We repeat at this point that η may be very strongly dependent on ν.

The generalization to a system with n interval variables is straightforward. To wit

$$\tau = \sum_{r=1}^{n} E_r p_r + K\nu\varepsilon \tag{37}$$

$$\dot{p}_r + \frac{E_r}{\eta_r} p_r = \dot{\varepsilon} \qquad r = 1, 2, \ldots, n \tag{38}$$

$$\dot{\nu} + b\exp\left(\sum_{r=1}^{n} \mu_r |p_r|\right)\nu = 0 \tag{39}$$

where μ_r may depend very strongly on ν as before. The physics of this dependence will be discussed at some length later in this section.

In studies on styrene–butadiene rubber (SBR), it has been found that the near-equilibrium part of the relaxation function is influenced to a significant effect by the crosslink density ν. Specifically, if $\Delta E(t)$ is the relaxation function minus its equilibrium part, and if ν_1 and ν_2 are two crosslink densities where ν_2 is greater than ν_1, then the following law is proposed:

$$\Delta E_2(t) = \Delta E_1\left[t\left(\frac{\nu_2}{\nu_1}\right)^n\right] \tag{40}$$

where n is a positive integer. This law was proposed by Plazek[5] on the basis of the observation by Chasset and Thirion[6] that if $\Delta E(t)$ is plotted *versus* $\log t$ for various values of ν, then an increase in ν shifts the function $E(t)$ to the left by a rigid body translation which is a function of ν. This function was found to be approximately of the type $A\nu^n$ where A is a constant. In the case of SBR, for instance, Arenz[7] found n to be of the order of 14 or 15 depending on the type of polymer at hand. It follows from equation (40) that the relaxation is actually accelerated by an increase in the crosslink density, as conjectured earlier.

In the context of our present deformation kinetics concepts, this phenomenon can be explained physically through recourse to the role of energy barriers in impeding the motion of the molecular chains of the skeleton.

Crosslinking has primarily two effects. One is to reduce the length of chains between crosslinks and the other is to reduce the number of free unattached chains, thus decreasing the density of the molecular liquid. The process of relaxation of a chain is impeded by the presence of the viscous-like milieu which consists primarily of unattached chains.

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 density of free chains, the less the probability of meeting an energy barrier.

Let the energy to overcome the resistance of a single 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 links including crosslinks as well as entanglements. Also let ν_e be the number of entanglements. Then

$$\nu_e + \nu = \nu_T \tag{41}$$

It is reasonable to assume that ν_T is constant in which case a linear relationship exists between ν_e and ν. Also if N is the number of a free chains then, on purely topological considerations, it is reasonable to expect a linear relationship of the type:

$$\nu_e = aN + b \tag{42}$$

where a and b are positive constants. Thus, from (41) and (42):

$$N = \frac{\nu_T - b}{a} - \frac{\nu}{a} \tag{43}$$

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

$$\varepsilon = \alpha'\theta\left(\frac{\nu_T - b}{a} - \frac{\nu}{a}\right) \tag{44}$$

where α' is a proportionality constant.

The above expression may be written in the form

$$\varepsilon = \varepsilon_0 - \gamma\nu \tag{45}$$

where ε_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 (45), the rate constant K_1 is given by:

$$K_1 = \frac{2\lambda}{\tau}\exp\left(-\frac{\varepsilon_0 - \gamma\nu}{\kappa T}\right)\sum_r \frac{1}{\alpha}\exp(-\beta\varepsilon_i^r) \tag{46}$$

The above equation may be written in the form:

$$K_1 = K_1^0 \exp(\gamma\nu/\kappa T) \tag{47}$$

where K_1^0 is a reference value of K_1.

Equation (47) is instrumental in determining the effect of crosslink density in the near-equilibrium part of the relaxation function. To determine this relationship we note that the viscosity coefficient η in equation (31) is given by:

$$\eta = \frac{1}{K_1 K_2} \tag{48}$$

a relation which is deducible from the linearized form of equation (24), and is essentially equation (19).

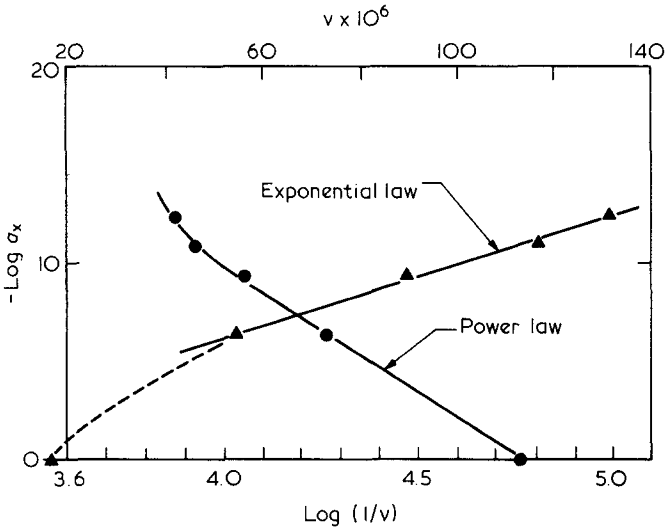

Figure 6 Power and exponential laws for shift function a_x (data from Arenzon SBR[7])

Thus, $1/\eta$ as it appears in equation (35) is given by equation (49) where:

$$\frac{1}{\eta}=K_2K_1^0\exp(\gamma\nu/\kappa T) \qquad (49)$$

or

$$\frac{1}{\eta}=\frac{1}{\eta_0}\exp(\gamma\nu/\kappa T) \qquad 50)$$

where η_0 is the viscosity of the molecular liquid when the crosslink density ν is equal to zero.

Again with reference to equation (49), the non-equilibrium part of the relaxation modulus at $\nu=0$, denoted here by ΔE°, is given by the relation:

$$\Delta E^\circ(t)=E_1^\circ\exp(-\alpha^\circ T) \qquad (51)$$

where $\alpha^\circ=E_1^\circ/\eta_0$.

At some other value of the crosslink density let the non-equilibrium part of the relaxation modulus be $\Delta E(t)$ where:

$$\Delta E=E_1e^{-\alpha t} \qquad (52)$$

and

$$\alpha=\alpha_0\exp(\gamma\nu/\kappa T) \qquad (53)$$

Since E_1, as opposed to η, is likely to be insensitive to changes in ν, then it follows from (52) and (53) that:

$$\Delta E(T)=\Delta E^\circ[t\exp(\gamma\nu/\kappa T)] \qquad (54)$$

The above equation has the general features of equation (40), except that the shift factor is an exponential rather than a power function of ν. Both functions are shown in *Figure 6* vis-à-vis experimental data obtained by Arenz[7]. It may be observed that the power function favours lower values of ν whereas the exponential function favours higher values of ν. Since the measurement of ν becomes more accurate as ν increases, the exponential form of the shift factor seems preferable in the present instance.

Equations (37) to (39) may now be written in the following more explicit form:

$$\sigma=\sum_{r=1}^{r}E_rp_r+\kappa\nu\varepsilon \qquad (55)$$

$$\dot{p}_r+\left(\frac{E_r}{\eta_r^0}\right)\exp(\gamma_r\nu/\kappa T)p_r=\dot{\varepsilon} \qquad (56)$$

$$\dot{\nu}+b\exp\left(\sum_{r=1}^{r}\mu_r|p_r|\right)\nu=0 \qquad (57)$$

An explicit solution of the above set of equations under conditions of varying ε and/orν will be presented in a subsequent paper.

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