

A model for the long-term viscoelastic behavior of aging polymers

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A constitutive model is derived for the physical aging of amorphous polymers. The model is based on the concept of transient networks, where a viscoelastic medium is treated as a system of adaptive links which break and arise due to micro-Brownian motion. Loss and reformation rates for the adaptive links are assumed to depend on the free volume fractions which, in turn, are governed by some kinetic equations. The model permits the long-term viscoelastic behaviour to be predicted based on experimental data obtained in standard short-term creep and relaxation tests. To verify the constitutive equations, we compare results of a numerical simulation with experimental data for several polymers, and demonstrate fair agreement between observations and their prediction. © 1997 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

This paper is concerned with the long-term viscoelastic behaviour of physically aging polymers. We confine ourselves to the analysis of amorphous polymers at small strains when the mechanical response may be treated as linear.

Physical aging of amorphous and semicrystalline polymers has attracted essential attention in the past three decades (see, for example, Refs. ^{1–6}, to mention a few). Aging means changes in the viscoelastic response of specimens quenched from the glass transition temperature Θ_g to some temperature $\Theta < \Theta_g$ and annealed for a time t_e at temperature Θ before loading.

Experimental data obtained in static short-term tests demonstrate a significant dependence of relaxation moduli on the elapsed time t_e . These data show that aging of amorphous polymers at small strains affects mainly the relaxation (retardation) spectra, which implies an opportunity to construct a creep (relaxation) master curve using an arbitrary set of short-term creep (relaxation) curves measured at various elapsed times (the time-aging time superposition principle¹).

A most important question remains about physical meaning of the master curve. Comparing experimental data obtained in short- and long-term tests, Struik¹ demonstrated that the master curve did not predict correctly creep in poly(vinyl chloride) when the duration of the measurements is comparable with the characteristic time of aging. Similar results were exposed by Matsumoto⁷ for poly(ether imide) and polycarbonate and by Read *et al.*^{8–10} for polypropylene and poly(vinyl chloride). Thus, a problem arises as to how to transform a master curve in such a way to adequately describe the long-term creep (relaxation) in aging media.

Read *et al.*^{8,9} proposed an approach for predicting long-

term creep (up to 10^6 (s)) based on short-term data. This technique has two peculiarities: (i) in order to predict static creep (relaxation) curves, the method employs some parameters of the β -relaxation region, which can be found in high-frequency dynamic tests only; and (ii) good agreement between observations and their prediction is demonstrated only when an adjustable parameter is introduced into the model (see, for example, Figs. 11 and 12 in Ref. ⁸ and Figs. 8–10 in Ref. ⁹).

The objective of the present paper is to derive constitutive equations which would correctly predict the long-term viscoelastic behaviour of amorphous polymers. Our purpose is to develop a model that may be employed in applied studies to estimate the effect of material aging on the mechanical response based on 'standard' tests. Such a model should be a relatively simple to carry out numerical analysis, and it should contain adjustable parameters to be determined in mechanical short-term tests. From this standpoint, the model^{8–10} has a serious drawback, since it requires experimental data of high-frequency tests. On the other hand, since β processes affect physical aging in the α region, our neglect of their influence is a simplification that will be justified later by comparison of numerical prediction with experimental data.

To derive constitutive relationships, we refer to the concept of transient networks, where the processes of creation and annihilation of chains are governed by the free volume fraction. The theory of transient reversible networks was proposed by Green and Tobolsky¹¹ and was developed in a number of works (see, for example, Refs. ^{12–17}). A review of the temporal network theory can be found, *e.g.* in Ref. ¹⁸. A version of this concept was applied in Ref. ¹⁹ to describe the short-term response in aging polymers (both amorphous and semicrystalline).

Unlike previous studies, we intend to incorporate a model of adaptive links with the free volume theory²⁰. The free volume concept has been widely employed to analyze viscoelastic properties of aging media (see, for example, Refs. ^{1,2,21–23}). The novelty of our approach consists of the

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use of different free volumes for different kinds of adaptive links. A similar idea was proposed earlier by Aklonis²⁴, but in another context.

The exposition is organized as follows. We begin with a version of the model of adaptive links and establish some connections between the rates of breakage and formation of new links. As a result, we arrive at differential equations for the numbers of links of various kinds, similar to equations in population dynamics. Coefficients in these equations are assumed to depend on the total free volume fraction, which equals the sum of the free volume fractions for different kinds of links. Afterwards, we introduce kinetic equations for free volume fractions and compare the results of the numerical analysis with experimental data for several polymeric materials. Finally, we determine adjustable parameters of the model by fitting data obtained in short-term creep and relaxation tests, calculate the material response in long-term tests, and validate the model by comparing the results of the numerical simulation with experimental data.

A MODEL OF ADAPTIVE LINKS

According to the concept of transient reversible networks¹⁷, a viscoelastic medium is treated as a network consisting of polymeric chains connected to junctions by sticky functional groups. An active chain (both ends of which are connected to separate junctions) is modelled as an elastic spring (link). The snapping of one end of an active chain from a junction is tantamount to the breakage of the link. When a dangling chain captures one of the junctions in its neighbourhood, a new adaptive link is assumed to be created.

It is supposed that M different kinds of links exist which correspond to M different relaxation times. Referring to the polymer dynamics theory, we assume that a random walk of chain molecules is determined by potentials that are characterized by several length scales: bond length, persistence length, coil diameter, etc.²⁵. From this standpoint, any kind of adaptive link may be treated as corresponding to interactions between chains with some characteristic length.

We denote by $X_m(t, \tau)$ the number of links of the m th kind which have arisen before instant τ and exist at instant t , and by \bar{X}_0 the number of initial links not involved in the reformation process. The quantities $X_m(t, \tau)$ and \bar{X}_0 are determined per unit volume in the reference configuration. We introduce relative rates of reformation

$$\gamma_m(\tau) = \frac{1}{\bar{X}_m} \frac{\partial X_m}{\partial \tau}(\tau, \tau) \quad (1)$$

where $\bar{X}_m = X_m(0, 0)$, and the breakage functions $g_m(t, \tau)$ which equal the relative number of adaptive links of the m th kind existing at instant τ and broken before instant t . One can write

$$\begin{aligned} X_m(t, 0) &= X_m(0, 0)[1 - g_m(t, 0)] = \bar{X}_m[1 - g_m(t, 0)] \\ \frac{\partial X_m}{\partial \tau}(t, \tau) &= \frac{\partial X_m}{\partial \tau}(\tau, \tau)[1 - g_m(t, \tau)] = \bar{X}_m \gamma_m(\tau)[1 - g_m(t, \tau)] \end{aligned} \quad (2)$$

Substitution of the expressions shown as equation (2) into the formula

$$X_m(t, t) = X_m(t, 0) + \int_0^t \frac{\partial X_m}{\partial \tau}(t, \tau) d\tau$$

yields

$$X_m(t, t) = \bar{X}_m \left\{ 1 - g_m(t, 0) + \int_0^t \gamma_m(\tau)[1 - g_m(t, \tau)] d\tau \right\} \quad (3)$$

The balance equation (3) is analogous to integral equations developed by Yamamoto¹³, and Tanaka and Edwards¹⁷. However, two aspects should be emphasized which distinguish our approach from conventional network theories.

- (1) Equation (3) is derived for the function X_m of two instants, t and τ , while the standard conservation equation is written for the chain-distribution function which depends on the current instant t and the end-to-end vector.
- (2) Equation (3) can be solved explicitly (see below), while conventional equations for the chain-distribution function do not permit analytical solutions to be found even in the simplest cases.

At the beginning, we consider non-aging viscoelastic media with time-independent mechanical properties. This means that

$$X_m(t, t) = \bar{X}_m, \quad \gamma_m(t) = \gamma_{m0}, \quad g_m(t, \tau) = g_{m0}(t - \tau) \quad (4)$$

It follows from equations (3) and (4) that

$$g_{m0}(t) = \gamma_{m0} \int_0^t [1 - g_{m0}(\tau)] d\tau$$

Differentiation of this equality implies that

$$\frac{dg_{m0}}{dt}(t) = \gamma_{m0}[1 - g_{m0}(t)], \quad g_{m0}(0) = 0 \quad (5)$$

Solving equation (5), we find that

$$g_{m0}(t) = 1 - \exp(-\gamma_{m0}t) \quad (6)$$

We substitute the expression shown as equation (6) into equation (2), use equations (4), and obtain

$$X_m(t, 0) = \bar{X}_m \exp(-\gamma_{m0}t),$$

$$\frac{\partial X_m}{\partial \tau}(t, \tau) = \bar{X}_m \gamma_{m0} \exp[-\gamma_{m0}(t - \tau)] \quad (7)$$

Combining equation (4) and (7) with the formula

$$X_m(t, \tau) = X_m(t, t) - \int_\tau^t \frac{\partial X_m}{\partial s}(t, s) ds$$

we find that the total number of adaptive links (per unit volume) arisen before instant τ and existing at instant t

$$X(t, \tau) = \bar{X}_0 + \sum_{m=1}^M X_m(t, \tau) \quad (8)$$

is calculated as

$$X(t, \tau) = \bar{X} \left\{ \eta_0 + \sum_{m=1}^M \eta_m \exp[-\gamma_{m0}(t - \tau)] \right\} \quad (9)$$

where

$$\bar{X} = \sum_{m=0}^M \bar{X}_m, \quad \eta_m = \frac{\bar{X}_m}{\bar{X}} \quad (10)$$

In linear viscoelasticity, the function $X(t, \tau)$ coincides with the relaxation kernel of a viscoelastic medium (see, for example, Ref. ²⁶). According to equation (9), the relaxation kernel of an arbitrary non-aging viscoelastic material can be

presented in the form of a truncated Prony series with positive coefficients.

Let us consider a subsystem of a system of adaptive links of the m th kind, which contains $\nu_m(\tau)$ links at instant τ , and calculate the number of links $\nu_m(t)$ in this subsystem at an arbitrary instant t . By analogy with equation (2), we write

$$\nu_m(t) = \nu_m(\tau)[1 - g_m(t, \tau)] \quad (11)$$

Differentiation of equation (11) with use of equations (4) and (5) implies that

$$\frac{1}{\nu_m(t)} \frac{d\nu_m}{dt}(t) = -\gamma_{m0} \quad (12)$$

According to equation (12), equation (5) means that for any subsystem in a system of adaptive links of the m th kind, the relative rate of breakage equals γ_{m0} .

Our aim now is to account for the effect of aging on the relaxation modulus. For aging viscoelastic media, equations (4) are not valid, and the balance equation (3) contains three unknown functions $X_m(t, t)$, $\gamma_m(t)$, and $g_m(t, \tau)$.

Two main approaches to the analysis of equation (3) may be distinguished. According to the first (see, for example, Refs. 17,27), the chain generation rates γ_m and the chain breakage rates $\partial g_m / \partial t$ are prescribed as functions of the current state of the transient network, while equation (3) determines the number of active chains $X_m(t, t)$.

According to the other approach, the breakage functions $g_m(t, \tau)$ are assumed to satisfy the partial differential equation (5)

$$\frac{\partial g_m}{\partial t}(t, \tau) = -\gamma_m(t)[1 - g_m(t, \tau)], \quad g_m(\tau, \tau) = 0 \quad (13)$$

with time-dependent coefficients $\gamma_m(t)$. Given reformation rates $\gamma_m(t)$, equation (13) is treated as a governing equation for the breakage functions $g_m(t, \tau)$. After solving this equation, equation (3) may be employed to calculate the total number of adaptive links $X_m(t, t)$ of the m th kind.

Following this approach, we find from equations (11) and (13) that the functions

$$n_m(t) = \frac{X_m(t, 0)}{\bar{X}_m}, \quad N_m(t, \tau) = \frac{1}{\bar{X}_m} \frac{\partial X_m}{\partial \tau}(t, \tau) \quad (14)$$

satisfy the differential equations

$$\frac{1}{n_m(t)} \frac{dn_m}{dt}(t) = -\gamma_m(t), \quad n_m(0) = 1, \\ \frac{1}{N_m(t, \tau)} \frac{\partial N_m}{\partial t}(t, \tau) = -\gamma_m(t), \quad N_m(\tau, \tau) = \gamma_m(\tau) \quad (15)$$

It follows from equation (15) that the breakage and reformation of adaptive links in an aging viscoelastic medium are determined by the functions $\gamma_m(t) = T_m^{-1}(t)$, where T_m is the m th relaxation time. With reference to the time-temperature superposition principle (see, for example Ref. 28), the relaxation times T_m are assumed to change in time similarly to each other, which means that the shift factor

$$a(t) = \frac{T_m(t)}{T_{m0}} \quad (16)$$

is independent of the index m . Equation (16) implies similarity of the reformation rates as well

$$\gamma_m(t) = \frac{\gamma_{m0}}{a(t)} \quad (17)$$

According to equation (17), the physical aging of polymers is determined by the function $a(t)$. The logarithmic derivative of this function, the so-called aging rate

$$\tilde{\mu} = -\frac{d \log a}{d \log t} \quad (\log = \log_{10})$$

was introduced by Struik¹ and used in a number of studies dealing with the mechanical and dielectric response in aging polymers. The functions $a(t)$ and $\tilde{\mu}(t)$, treated as measures of the material aging, have two obvious advantages: (i) they are easy to be determined using experimental data obtained in standard creep (relaxation) tests for various elapsed times; and (ii) the aging rate $\tilde{\mu}$ depends feebly on the elapsed time and the temperature Θ of annealing (see Ref. 1). The main drawback of these measures is that they do not reveal physical reasons for the aging process. To refine this approach, Struik^{22,23} established a correlation between changes in the free volume fraction f and the shift factor a . To develop the Struik model, we consider the free volume concept in more detail.

A MODEL OF THE FREE VOLUME

According to the conventional free volume theory (see, for example, Ref. 21), some volume V is ascribed to each polymeric chain. This volume consists of two parts: the occupied volume V_o and the free volume V_f

$$V = V_o + V_f$$

Since the quantities V , V_o , and V_f are not observed directly, it is convenient to write this equality for specific volumes (per unit mass)

$$v = v_o + v_f \quad (18)$$

The left-hand side of equation (18) is determined in standard dilatometric tests, but the amounts v_o and v_f cannot be measured separately.

To distinguish the occupied volume v_o and the free volume v_f , we assume that under isothermal loading at a constant temperature Θ , these quantities tend to some equilibrium values $\bar{v}_o(\Theta)$ and $\bar{v}_f(\Theta)$, but the rates at which the equilibria are approached essentially differ. After quenching from some temperature $\Theta_1 > \Theta$ to a temperature Θ , the rate of change in v_o is supposed to be large, while the rate of change in v_f is comparatively small. Since we are concerned with rather slow processes (aging), we assume that the occupied volume v_o immediately reaches its equilibrium value

$$v_o(t_e) = \bar{v}_o(\Theta), \quad t_e > 0$$

where t_e is the time elapsed after quenching.

The volume \bar{v}_o is assumed to increase linearly with temperature

$$\bar{v}_o(\Theta) = v_o(\Theta_r)[1 + \tilde{\alpha}(\Theta - \Theta_r)] \quad (19)$$

where $\bar{v}_o(\Theta_r)$ is the specific occupied volume at the reference (e.g. room) temperature Θ_r , and $\tilde{\alpha}$ is the coefficient of thermal expansion. In the general case, the specific free volume v_f is a function of elapsed time t_e and temperature Θ . Expanding this function into the Taylor series in temperature and omitting the non-linear terms (as has already been done with equation (19)), we obtain

$$v_f(\Theta, t_e) = v_f^0(t_e) + \frac{\partial v_f}{\partial t_e}(\Theta_r, t_e)(\Theta - \Theta_r)$$

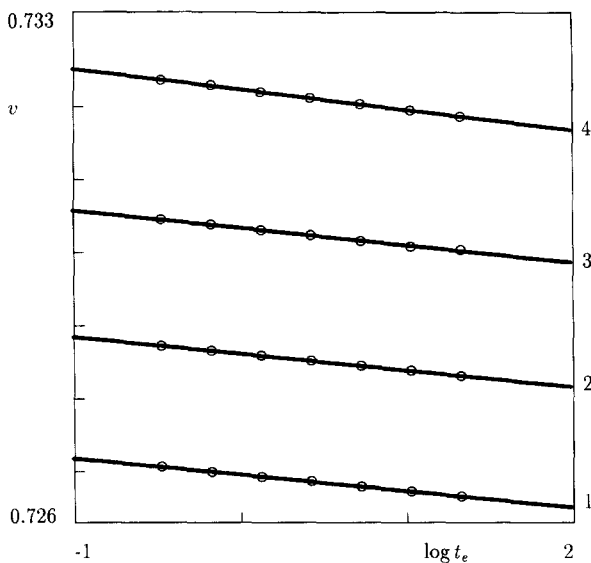


Figure 1 The specific volume v ($\text{cm}^3 \text{g}^{-1}$) versus elapsed time t_e (h) for poly(vinyl chloride) Solvay quenched from 100°C to a temperature $\Theta^\circ\text{C}$. Circles, experimental data obtained by Struik²³. Curve 1, $\Theta = 40$; curve 2, $\Theta = 50$; curve 3, $\Theta = 60$; curve 4, $\Theta = 70$. The solid lines represent their approximation by equation (20) with the following parameters.

Θ	c_1	$10^4 c_2$
40.0	0.7267	-2.2364
50.0	0.7283	-2.2946
60.0	0.7300	-2.3772

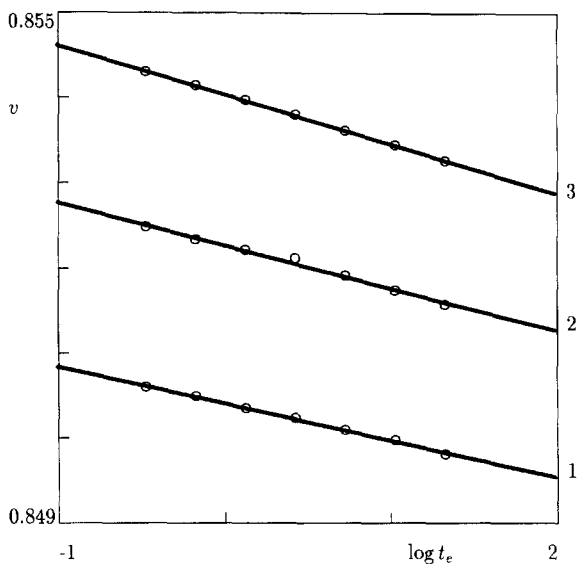


Figure 2 The specific volume v ($\text{cm}^3 \text{g}^{-1}$) versus elapsed time t_e (h) for polycarbonate Macrolon-8032 quenched from 155°C to a temperature $\Theta^\circ\text{C}$. Circles, experimental data obtained by Struik²³. Curve 1, $\Theta = 100$; curve 2, $\Theta = 110$; curve 3, $\Theta = 120$. The solid lines represent their approximation by equation (20) with the following parameters.

Θ	c_1	$10^4 c_2$
100.0	0.8504	-4.3539
110.0	0.8523	-5.0004
120.0	0.8540	-5.8037

where $v_f^0(t_e) = v_f(t_e, \Theta_r)$. This equality, together with equations (18) and (19), implies that

$$v(\Theta, t_e) = \bar{v}_0(\Theta_r)[1 + \alpha(\Theta - \Theta_r)] + v_f^0(t_e) \quad (20)$$

where

$$\alpha = \tilde{\alpha} + \frac{1}{\bar{v}_0(\Theta_r)} \frac{\partial v_f}{\partial t_e}(\Theta_r, t_e)$$

Experimental data for poly(vinyl chloride) and polycarbonate plotted in Figures 1 and 2 together with their approximations by the linear function

$$v = c_1 + c_2 \log t_e \quad (21)$$

demonstrate that the adjustable parameter

$$c_2 = \frac{\partial v}{\partial \log t_e}$$

depends weakly on Θ (it increases by about 20% with the increase of temperature in the range of test temperatures). For simplicity, we will neglect this dependence, which is equivalent to the assumption that the coefficient of thermal expansion α in equation (20) is constant. To determine the α value, we plot the specific volume $v(\Theta, t_e)$ at a fixed elapsed time t_e versus temperature Θ , and approximate the experimental data by linear dependencies; see Figure 3.

It follows from equation (20) that

$$v(\Theta_r, \infty) = \bar{v}_0(\Theta_r) + v_f^0(\infty) \quad (22)$$

Subtracting equation (22) from equation (20), we obtain

$$\begin{aligned} \Delta v_f(t_e) &= v_f^0(t_e) - v_f^0(\infty) \\ &= v(\Theta, t_e) - v(\Theta_r, \infty) - \alpha(\Theta - \Theta_r)\bar{v}_0(\Theta_r) \end{aligned}$$

Dividing the increment of the free volume Δv_f by the specific volume v , we calculate the increment of the free volume fraction

$$\Delta f(t_e) = 1 - \frac{v(\Theta_r, \infty)}{v(\Theta, t_e)} - \alpha(\Theta - \Theta_r) \frac{\bar{v}_0(\Theta_r)}{v(\Theta_r, t_e)} \quad (23)$$

To describe changes of the free volume fraction in time, we suppose that the total increment of the free volume equals the sum of the increments of the free volumes for all kinds of polymeric chains (adaptive links)

$$\Delta f = \sum_{m=1}^M \Delta f_m \quad (24)$$

Here Δf_m is the increment of the free volume fraction of the

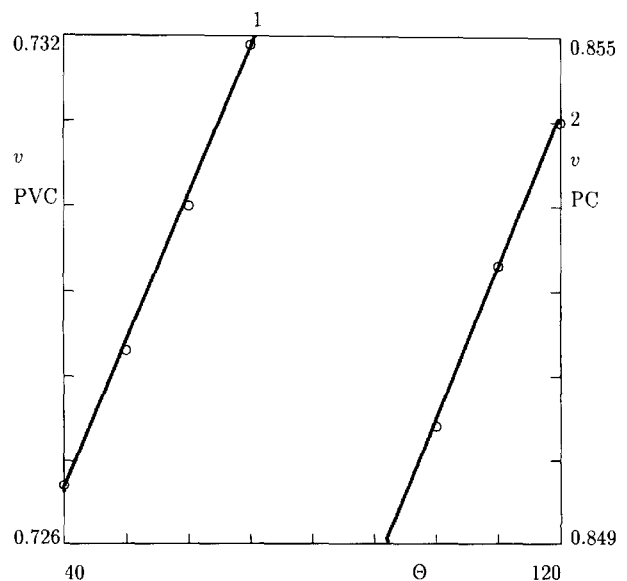


Figure 3 The specific volume v ($\text{cm}^3 \text{g}^{-1}$) at $t_e = 1$ (h) versus temperature $\Theta^\circ\text{C}$ for (curve 1) poly(vinyl chloride) Solvay, and (curve 2) polycarbonate Macrolon-8032. Circles, experimental data obtained by Struik²³. The solid lines represent their approximation by linear functions with $\alpha = 1.73 \times 10^{-4}$ (1/K) for poly(vinyl chloride) and $\alpha = 1.80 \times 10^{-4}$ (1/K) for polycarbonate. The former value is in agreement with $\alpha = 2.07 \times 10^{-4}$ (1/K) found for poly(vinyl chloride) Solvic 229 by Schwarzl and Zahradnik²⁹

m th kind of links

$$\Delta f_m(t_e) = \frac{v_{f,m}(t_e) - v_{f,m}(\infty)}{v(\Theta, t_e)} \quad (25)$$

where $v_{f,m}$ is the free volume corresponding to an adaptive link of the m th kind. Equation (24) allows us (at least, phenomenologically) to account for the effect of β processes on the viscoelastic response in the α region by assuming that some kinds of adaptive links have characteristic times located in the β region.

Since the free volume fraction is small compared with unity and the effect of thermal expansion is rather weak, the specific volume $v(\Theta, t_e)$ in equation (25) can be replaced by its limiting value at room temperature $v(\Theta_r, \infty)$. As a result, we obtain

$$\Delta f_m(t_e) = \frac{v_{f,m}(t_e) - v_{f,m}(\infty)}{v(\Theta_r, \infty)} \quad (26)$$

With reference to Kovacs³⁰, we describe changes in the free volume $v_{f,m}$ by the kinetic equation

$$\frac{dv_{f,m}}{dt_e}(t_e) = -\Gamma_m[v_{f,m}(t_e) - v_{f,m}(\infty)] \quad (27)$$

where Γ_m are rates of approaching the equilibria.

Unlike the original Kovacs model and its refinements (see Refs. ^{2,21,24,31} and references therein), we do not assume that the quantities Γ_m depend on the free volume, but treat them as constants. This simplification allows us to reduce significantly the number of adjustable parameters and to determine these parameters by fitting data in the standard dilatometric tests. On the other hand, our assumption neglects non-linearities in the volume recovery kinetics. The non-linear effects are small in a reasonable, from the engineering standpoint, interval of time (ranged, for example, from 10^6 to 10^7 (s) when the difference $\Theta_g - \Theta$ is rather large (e.g. exceeds 5°C for poly(vinyl acetate); see Ref. ³⁰). For smaller temperature jumps $\Theta_g - \Theta$, the non-linearity reveals itself earlier, but in this case the entire approach becomes questionable, since in the non-linear region the kinetics of changes in the relaxation spectra decouple from the kinetics of volume recovery; see Refs. ^{32,33}. Since experimental knowledge about the decoupling phenomenon is quite limited (see a discussion of this question in Ref. ³⁴), we confine ourselves to the linear region of volume recovery (this is the case, for example, when the material in question is cooled by tens of degrees, which is of essential interest for applications in polymer engineering). To account for the entire range of temperatures below Θ_g , non-linear constitutive equations should be analyzed where the kinetic coefficients Γ_m are functions of temperature and the free volume fraction (see Ref. ²¹).

Integration of equation (27) results in

$$v_{f,m}(t_e) - v_{f,m}(\infty) = [v_{f,m}(0) - v_{f,m}(\infty)] \exp(-\Gamma_m t_e)$$

Substitution of this expression into equations (24) and (25) implies that

$$\Delta f(t_e) = \sum_{m=1}^M \zeta_m \exp(-\Gamma_m t_e) \quad (28)$$

where

$$\zeta_m = \frac{v_{f,m}(0) - v_{f,m}(\infty)}{v(\Theta_r, \infty)}$$

Given rates of approaching the equilibria Γ_m ($m = 1, \dots, M$), the adjustable parameters ζ_m are determined by fitting experimental data; see Figure 4. This figure demonstrates that equation (28) ensures the same level of accuracy in fitting data for poly(vinyl chloride) and polycarbonate as

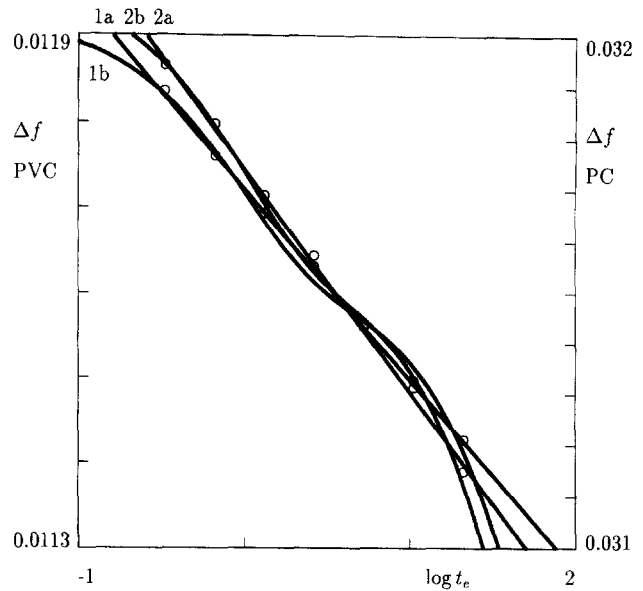


Figure 4 The increment of the free volume fraction Δf versus elapsed time t_e (h) for poly(vinyl chloride) Solvay quenched from 100°C (curves 1) and polycarbonate Macrolon-8032 quenched from 155°C (curves 2). Circles, treatment of experimental data obtained by Struik²³. The solid lines represent approximations by (a) equation (29) with $\beta_1 = 0.0117$, $\beta_2 = -2.2364 \times 10^{-4}$ for poly(vinyl chloride) and $\beta_1 = 0.0317$, $\beta_2 = -4.3539 \times 10^{-4}$ for polycarbonate (PC); and (b) equation (28) with the following parameters.

$\Gamma_m(\text{h}^{-1})$	ζ_m , PVC	ζ_m , PC
0.0001	0.0107	0.0296
0.0100	0.0009	0.0019
1.0000	0.0003	0.0005

the conventional linear dependence

$$\Delta f(t_e) = \beta_1 + \beta_2 \log t_e \quad (29)$$

An important drawback of equation (28) is that it requires a larger number of adjustable parameters to be found (compared to equation (29)). Its significant advantage lies in the opportunity to treat changes in the free volume fraction as kinetic processes of the first order. It is worth noting that some expression similar to equation (28) was proposed by Knauss and Emri³⁵ for the so-called thermal creep function.

We assume now that the shift factor a in equations (16) and (17) is a function of the excess free volume fraction Δf . A similar approach was employed in several recent studies dealing with the non-linear viscoelastic response in solid polymers (see, for example, Refs. ³⁵⁻³⁷). Unlike those works, where the shift factor a was expressed in terms of the free volume fraction f with the use of the Doolittle equation, we set

$$a_r(\Theta, t_e) = a_{r,1}(\Theta) a_{r,2}(\Delta f) \quad (30)$$

where the thermal shift factor $a_{r,1}(\Theta)$ determines the shift of a creep (relaxation) curve obtained after annealing for a time t_e^0 at a temperature Θ with respect to the reference curve obtained after annealing for a time t_e^0 at a temperature Θ^0 , and $a_{r,2}(\Delta f)$ determines the shift of a creep (relaxation) curve obtained after annealing for a time t_e at a temperature Θ^0 with respect to the reference curve. We assume an Arrhenius formula for the shift factor $a_{r,1}$

$$\log a_{r,1}(\Theta) = \frac{\Delta H}{R \ln 10} \left(\frac{1}{\Theta} - \frac{1}{\Theta^0} \right) \quad (31)$$

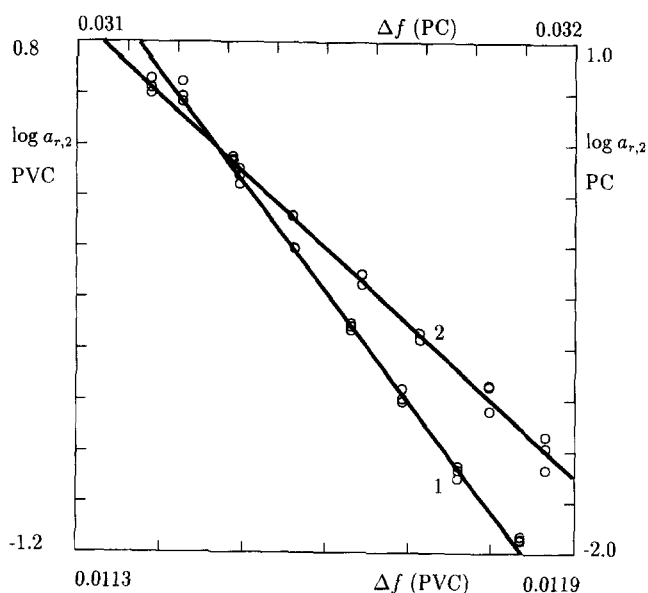


Figure 5 The relative shift factor $a_{r,2}$ [reduced to $t_e^0 = 5.33$ (h)] versus the increment of the free volume fraction Δf for poly(vinyl chloride) Solvay quenched from 100°C to 40, 50 and 60°C (curve 1), and for polycarbonate Macrolon-8032 quenched from 155°C to 100, 110 and 120°C (curve 2). Circles, treatment of experimental data obtained by Struik²³. The solid lines represent the approximation of the experimental data by equation (32) with $C_1 = 49.843$, $C_2 = -4.3111 \times 10^4$ for poly(vinyl chloride) and $C_1 = 84.553$, $C_2 = -2.6905 \times 10^4$ for polycarbonate

where ΔH is the activation enthalpy, and R is the Boltzmann constant, and propose a linear dependence for the shift factor $a_{r,2}$,

$$\log a_{r,2}(\Delta f) = C_1 + C_2 \Delta f \quad (32)$$

where C_1 and C_2 are temperature-independent parameters, which are determined by fitting experimental data obtained in dilatometric and creep tests. A weak dependence of the adjustable parameters C_1 and C_2 on temperature is confirmed by experimental data for poly(vinyl chloride) and polycarbonate, depicted in Figure 5.

To check equation (30), we begin with experimental data for polystyrene specimens quenched from the glass transition temperature $\Theta_g = 100^\circ\text{C}$ to $\Theta_1 = 90^\circ\text{C}$ and $\Theta_2 = 95^\circ\text{C}$ and annealed for a time t_e . According to equation (30), the curves $\log a_{r,2}$ versus $\log t_e$ determined at different temperatures Θ_k should coincide after a vertical shift by $\log a_{r,1}$. This assertion is confirmed with a high level of accuracy by data plotted in Figure 6.

We proceed now with data obtained in short-term relaxation tests for polystyrene specimens quenched from $\Theta_g = 100^\circ\text{C}$ to $\Theta_1 = 56^\circ\text{C}$ and $\Theta_2 = 90^\circ\text{C}$ and annealed for a time t_e . According to equation (30), to construct a master curve, it suffices to shift along the time-axis relaxation curves measured at various temperatures. This statement is confirmed by data depicted in Figure 7.

CONSTITUTIVE EQUATIONS FOR A VISCOELASTIC MEDIUM

We confine ourselves to relatively slow processes, the characteristic times of which exceed essentially the time necessary for stress in a broken link to relax, and assume that the strain energy density of the entire transient network equals the sum of strain energy densities for active chains; see Ref. 17.

An adaptive link of the m th kind is modelled as a linear elastic spring with a rigidity c . The natural (stress-free)

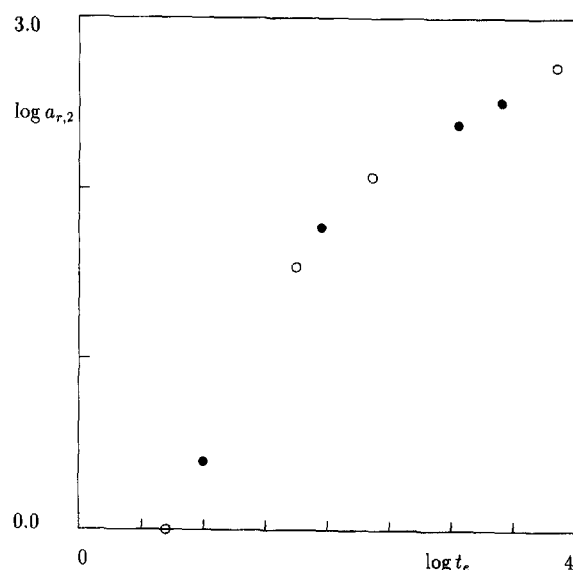


Figure 6 The relative shift factor $a_{r,2}$ versus the elapsed time t_e (min) for polystyrene quenched from 100°C to 90°C (empty circles) and 95°C (filled circles). The parameter $a_{r,2}$ is calculated for $t_e^0 = 5$ (min) at $\Theta = 90^\circ\text{C}$ and for $t_e^0 = 10$ (min) at $\Theta = 95^\circ\text{C}$. Circles, treatment of experimental data obtained by Plazek *et al.*³⁸. Filled circles are shifted along the vertical axis by $\log a_{r,1} = 0.4$ to construct a smooth master curve. According to equation (31), the latter value implies that $\Delta H = 48.92$ (kcal mol⁻¹)

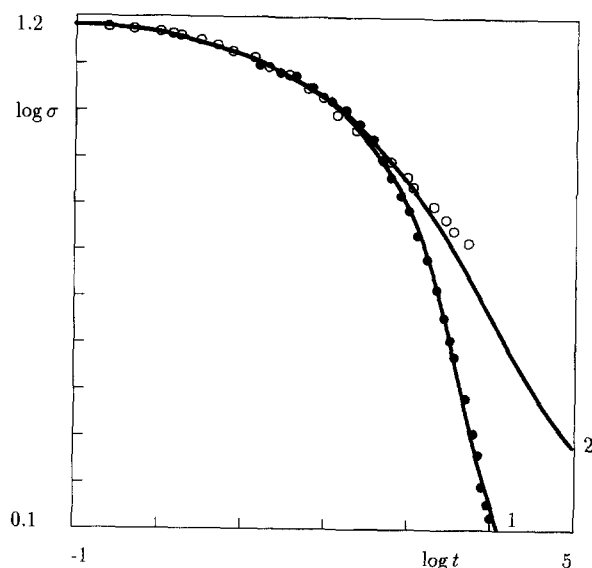


Figure 7 The stress σ (MPa) versus time t (min) for polystyrene quenched from 100°C and annealed for $t_e^0 = 15$ (h). The master curve (reduced to $\Theta = 56^\circ\text{C}$) is constructed using experimental data obtained by Matsuoka *et al.*³⁹ at temperatures $\Theta_1 = 56^\circ\text{C}$ (empty circles) and $\Theta_2 = 90^\circ\text{C}$ (filled circles). The relaxation curve measured at Θ_2 is shifted horizontally by $\log a_{r,1} = 1.41$ which corresponds to $\Delta H = 22.72$ (kcal mol⁻¹). Curve 1, approximation of the short-term master curve by equation (45) with $\mu = 3.06$ (GPa) and

η_m	γ_{m0} (min ⁻¹)
0.1299	0.00005
0.4560	0.00050
0.1983	0.00500
0.1268	0.05000
0.0749	0.50000

Curve 2, prediction of the long-term relaxation curve at $\Theta = 56^\circ\text{C}$

configuration of an adaptive link which merges with the system at an instant τ coincides with the actual configuration of the network at that instant. This assertion is equivalent to the hypothesis that the stress in a dangling chain is totally

relaxed before this chain catches a new sticky junction. The potential energy of an active chain is calculated as

$$w_m(t, \tau) = \frac{1}{2} c \epsilon_*^2(t, \tau) \quad (33)$$

where $\epsilon_*(t, \tau)$ is the strain at the current instant t in a link created at instant τ .

Let $\bar{l}(\tau)$ be the unit vector directed along the link at the instant of its formation, and $\hat{\epsilon}(t)$ the (macroscopic) strain tensor in a viscoelastic medium at instant t . One can write

$$\epsilon_*(t, \tau) = \bar{l}(\tau) \cdot [\hat{\epsilon}(t) - \hat{\epsilon}(\tau)] \cdot \bar{l}(\tau) \quad (34)$$

where the dot stands for the inner product. For uniaxial deformation, we can set

$$\hat{\epsilon}(t) = \epsilon(t) \bar{e} \bar{e} \quad (35)$$

where \bar{e} is the unit eigenvector of the strain tensor. Substitution of equations (34) and (35) into equation (33) implies that

$$w_m(t, \tau) = \frac{1}{2} c [\epsilon(t) - \epsilon(\tau)]^2 \sin^4 \vartheta \quad (36)$$

where the angles ϕ and ϑ determine the position of the vector $\bar{l}(\tau)$ in a spherical coordinate frame connected with the vector \bar{e} . Summing up the potential energies, and assuming that the medium is isotropic (which means that no preferable direction exists for adaptive links), we find that the strain energy density $d\bar{W}_m(t, \tau)$ (per unit volume in the reference configuration) of adaptive links of the m th kind that have arisen within the interval $\tau, \tau + d\tau$ is determined as follows:

$$d\bar{W}_m(t, \tau) = \frac{c}{2} [\epsilon(t) - \epsilon(\tau)]^2 \frac{\partial X_m}{\partial \tau}(t, \tau) d\tau \times \frac{\int_0^{2\pi} d\phi \int_0^\pi \sin^5 \vartheta d\vartheta}{\int_0^{2\pi} d\phi \int_0^\pi \sin \vartheta d\vartheta}$$

By analogy with equation (37), the strain energy density $\bar{W}_m(t, 0)$ (per unit volume in the reference configuration) of the initial links of the m th kind equals

$$\bar{W}_m(t, 0) = \frac{c}{2} \epsilon^2(t) X_m(t, 0) \frac{\int_0^{2\pi} d\phi \int_0^\pi \sin^5 \vartheta d\vartheta}{\int_0^{2\pi} d\phi \int_0^\pi \sin \vartheta d\vartheta} \quad (38)$$

Calculating the integrals in equation (37) and (38), we find that

$$\bar{W}_m(t, 0) = \frac{\bar{c}}{2} X_m(t, 0) \epsilon^2(t),$$

$$d\bar{W}_m(t, \tau) = \frac{\bar{c}}{2} \frac{\partial X_m}{\partial \tau}(t, \tau) [\epsilon(t) - \epsilon(\tau)]^2 d\tau \quad (39)$$

where $\bar{c} = (4/15)c$. Summing up the potential energies (equation (39)) for the adaptive links existing at an instant t , we obtain the total potential energy of the network

$$W(t) = \frac{\bar{c}}{2} \bar{X}_0 \epsilon^2(t) + \frac{\bar{c}}{2} \sum_{m=1}^M \left\{ X_m(t, 0) \epsilon^2(t) + \int_0^t \frac{\partial X_m}{\partial \tau}(t, \tau) [\epsilon(t) - \epsilon(\tau)]^2 d\tau \right\}$$

Substitution of equations (10) and (15) into this equality

implies that

$$W(t) = \frac{\mu}{2} \left\langle \eta_0 \epsilon^2(t) + \sum_{m=1}^M \eta_m \{ n_m(t) \epsilon^2(t) + \int_0^t N_m(t, \tau) [\epsilon(t) - \epsilon(\tau)]^2 d\tau \} \right\rangle \quad (40)$$

where $\mu = \bar{c} \bar{X}$.

The stress $\sigma(t)$ is calculated as follows (see, for example, Ref. ⁴⁰)

$$\sigma(t) = \frac{\partial W(t)}{\partial \epsilon(t)} \quad (41)$$

Combining equations (40) and (41), we find that

$$\sigma(t) = \mu \left\{ \left[\eta_0 + \sum_{m=1}^M \eta_m n_m(t) \right] \epsilon(t) + \sum_{m=1}^M \eta_m \int_0^t N_m(t, \tau) [\epsilon(t) - \epsilon(\tau)] d\tau \right\}$$

Bearing in mind that

$$\eta_0 = 1 - \sum_{m=1}^M \eta_m$$

we obtain

$$\sigma(t) = \mu \left(\left(1 - \sum_{m=1}^M \eta_m [1 - n_m(t)] \right) \epsilon(t) + \sum_{m=1}^M \eta_m \int_0^t N_m(t, \tau) [\epsilon(t) - \epsilon(\tau)] d\tau \right) \quad (42)$$

Equation (42) provides the constitutive equation for a non-linear viscoelastic medium with a strain-dependent relaxation spectrum. The functions $n_m(t)$ and $N_m(t, \tau)$ in the right-hand side of equation (42) satisfy equation (15), where the reformation rates γ_m are determined according to equation (17). The parameters γ_{m0} in equation (17) equal the reformation rates in a medium quenched from the glass transition temperature Θ_g to the reference temperature Θ^0 and annealed for the reference time t_c^0 . The shift factor a_r in equation (17) is expressed in terms of the temperature Θ and the excess free volume fraction Δf with the use of equations (30)–(32), where the function Δf is calculated according to equation (28) or equation (29).

RELAXATION TESTS

To analyze the constitutive model equations (15) and (17), equations (28)–(32), and equation (42), we consider the standard tensile relaxation test for specimens quenched from the glass transition temperature Θ_g to a reference temperature Θ^0 and annealed for a time t_e

$$\epsilon(t) = \begin{cases} 0, & t < t_e \\ \epsilon, & t \geq t_e \end{cases} \quad (43)$$

Substitution of equation (43) into equation (42) yields

$$\sigma_{t_e}(t) = \mu \left\{ 1 - \sum_{m=1}^M \eta_m [1 - n_m(t)] \right\} \epsilon \quad (44)$$

where $\sigma_{t_c}(t) = \sigma(t + t_c)$. We begin with short-term tests, the duration of which is essentially less than the elapsed time t_c . In this case, we can set

$$a_r(\Theta, t + t_c) = a_r(\Theta, t_c) \quad (45)$$

Combining equation (17) and (45), we obtain

$$\gamma_m(t) = \frac{\gamma_{m0}}{a_r(\Theta, t_c)} \quad (46)$$

It follows from equation (15) and (46) that

$$n_m(t) = \exp\left[-\frac{\gamma_{m0}t}{a_r(\Theta, t_c)}\right]$$

Substitution of this expression into equation (44) implies that

$$\sigma_{t_c}(t) = \mu \left\{ 1 - \sum_{m=1}^M \eta_m \left[1 - \exp\left(-\frac{\gamma_{m0}t}{a_r(\tau, t_c)}\right) \right] \right\} \quad (47)$$

According to equation (47), a master curve can be constructed of a set of relaxation curves measured at various temperatures Θ for the same elapsed time t_c^0 and plotted in bilogarithmic coordinates. Approximating the master curve by a Prony series, we determine the Young's modulus μ and the material parameters η_m ; see curve 1 in Figure 7, where experimental data for polystyrene are presented.

Short-term relaxation curves, measured at a temperature Θ for different elapsed times t_c and plotted in bilogarithmic coordinates, can be shifted horizontally by $a_{r,2}(t_c)$ to construct a master curve. The shift factor $a_{r,2}$ is plotted in Figure 8, where the experimental data are approximated by the linear function

$$\log a_{r,2}(t_c) = b_1 + b_2 \log t_c \quad (48)$$

with adjustable parameters b_1 and b_2 . Since the function $a_{r,2}(t_c)$ is temperature-independent (see equations (26) and (32)), it determines also appropriate shifts of short-term relaxation curves at the reference temperature Θ^0 .

Finally, to calculate a long-term relaxation curve with given parameters μ , b_k , η_m , and γ_{m0} , we integrate ordinary

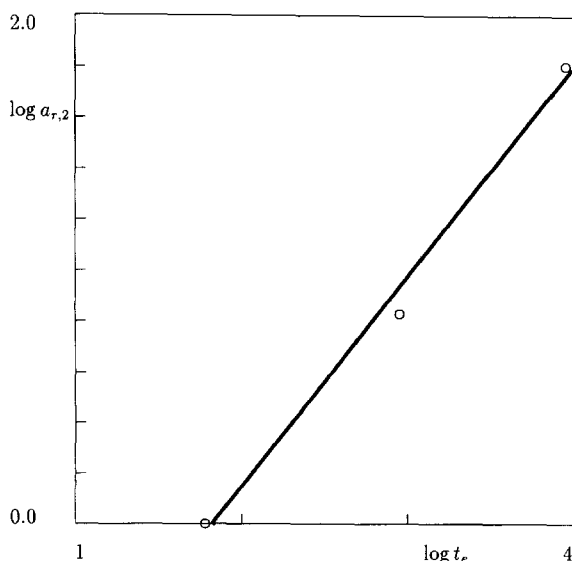


Figure 8 The shift factor $a_{r,2}$ [reduced to $t_c^0 = 1$ (h)] versus elapsed time t_c (min) for polystyrene quenched from $\Theta_g = 100^\circ\text{C}$ to $\Theta^0 = 90^\circ\text{C}$. Circles, treatment of experimental data obtained by Matsuoka *et al.*³⁹. The solid line represents the approximation of the experimental data by equation (48) with $b_1 = -1.5132$ and $b_2 = 0.8257$

differential equation (15), where the functions $\gamma_m(t)$ are determined by equations (17) and (48)

$$\gamma_m(t) = \frac{\gamma_{m0}}{10^{b_1} t^{b_2}} \quad (49)$$

and substitute the results obtained into equation (44). The long-term relaxation curve for polystyrene is plotted in Figure 7 (curve 2). The results of the numerical simulation demonstrate fair agreement with experimental data (empty circles), which means that the proposed model may be used to predict the response in aging specimens.

CREEP TESTS

To demonstrate the advantages of the model, we also predict strains in the standard creep tensile tests and compare results of numerical simulation with experimental data. A specimen is quenched from some temperature above the glass transition temperature Θ_g to a temperature Θ , annealed for a time t_c at the temperature Θ , and loaded by the stress

$$\sigma(t) = \begin{cases} 0, & t < t_c \\ \sigma, & t \geq t_c \end{cases} \quad (50)$$

According to equation (42) and (50), the strain $\epsilon_{t_c}(t) = \epsilon(t_c + t)$ is governed by the Volterra integral equation

$$\begin{aligned} & \left\{ 1 - \sum_{m=1}^M \eta_m [1 - n_m(t)] \right\} \epsilon_{t_c}(t) \\ & + \sum_{m=1}^M \eta_m \int_0^t N_m(t, \tau) [\epsilon_{t_c}(t) - \epsilon_{t_c}(\tau)] d\tau = \frac{\sigma}{\mu} \end{aligned} \quad (51)$$

In short-term tests, the shift factor a_r is independent of t (see equation (45)), the reformation rates are determined by equation (46), and the differential equations (15) are integrated explicitly

$$n_m(t) = \exp\left[-\frac{\gamma_{m0}t}{a_r(\Theta, t_c)}\right],$$

$$N_m(t, \tau) = \frac{\gamma_{m0}}{a_r(\Theta, t_c)} \exp\left[-\frac{\gamma_{m0}(t-\tau)}{a_r(\Theta, t_c)}\right]$$

Substituting these expressions into equation (51), we obtain, after simple algebra,

$$\epsilon_{t_c}(t) + \int_0^t \dot{Q}(t-\tau) \epsilon_{t_c}(\tau) d\tau = \frac{\sigma}{\mu} \quad (52)$$

where the relaxation measure $Q(t)$ equals

$$Q(t) = - \sum_{m=1}^M \eta_m \left[1 - \exp\left(-\frac{\gamma_{m0}t}{a_r(\Theta, t_c)}\right) \right] \quad (53)$$

and the superposed dot stands for the derivative with respect to time. The solution of equation (52) reads

$$\epsilon_{t_c}(t) = [1 + C(t)] \frac{\sigma}{\mu} \quad (54)$$

where the creep measure $C(t)$ is connected with the relaxation measure $Q(t)$ by the linear Volterra equations (see, for example, Ref. 26)

$$C(t) = -Q(t) - \int_0^t \dot{Q}(t-\tau) C(\tau) d\tau \quad (55)$$

$$Q(t) = -C(t) - \int_0^t \dot{C}(t-\tau) Q(\tau) d\tau \quad (56)$$

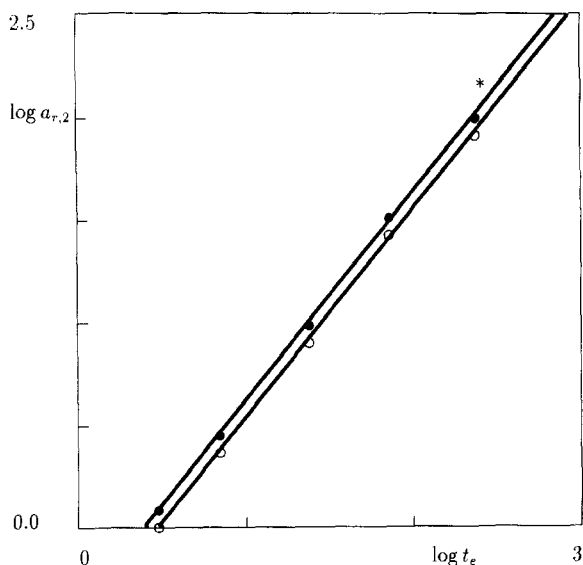


Figure 9 The shift factor $a_{r,2}$ [reduced to $t_e = 3(\text{h})$] versus the elapsed time t_e (h) for poly(vinyl chloride) Darvic quenched from 85 to 23°C. Empty circles, experimental data obtained by Dean *et al.*¹⁰. The solid line represents their approximation by equation (48) with $b_1 = -0.4881$ and $b_2 = 1.0146$. Filled circles, the shift factor $a_{r,2}$ [reduced to $t_e = 2.5(\text{h})$]. Asterisk, an experimental datum obtained by Read *et al.*⁹

We begin with a set of short-term creep curves $\epsilon_{t_c} = \epsilon_c(t)$ measured at the reference temperature Θ^0 for various elapsed times t_e . First, we construct a creep master curve by horizontal shifts of the creep curves and find the shift factor $a_{r,2}$ as a function of the elapsed time t_e . The function $a_{r,2}$ for poly(vinyl chloride) is plotted in Figure 9, together with its approximation by equation (48). The empty circles in Figure 9 are determined by constructing a master curve (reduced to $t_e^0 = 3$ (h)) based on experimental data provided by Dean *et al.*¹⁰. The adjustable parameters b_1 and b_2 are found to ensure the best fit of these data. Afterwards, we calculate the dependence $a_{r,2}(t_e)$ reduced to $t_e^0 = 2.5$ (h) (filled circles in Figure 9) and compare the numerical results with a datum obtained by Read *et al.*⁹ for the same material (asterisk). Small deviations between the predicted and measured quantities mean that the values of b_k are reliable.

We now approximate the short-term creep master curve (reduced to the reference elapsed time t_e^0) by equation (54), where the creep measure $C(t)$ is presented by a truncated Prony series

$$C(t) = \sum_{m=1}^M \chi_m [1 - \exp(-\gamma_{m0}t)] \quad (57)$$

Given M and the reformation rates γ_{m0} , the coefficients χ_m and the elastic modulus μ are found to ensure the best fit of the experimental data; see Figure 10.

To determine the relaxation measure $Q(t)$ corresponding to the creep measure (equation (57)), the integral equation (56) is solved. Combining equations (56) and (57), we find that

$$Q(t) = - \sum_{m=1}^M \chi_m [1 - \exp(-\gamma_{m0}t) - P_m(t)] \quad (58)$$

where the functions

$$P_m(t) = \gamma_{m0} \int_0^t \exp[-\gamma_{m0}(t-\tau)] Q(\tau) d\tau$$

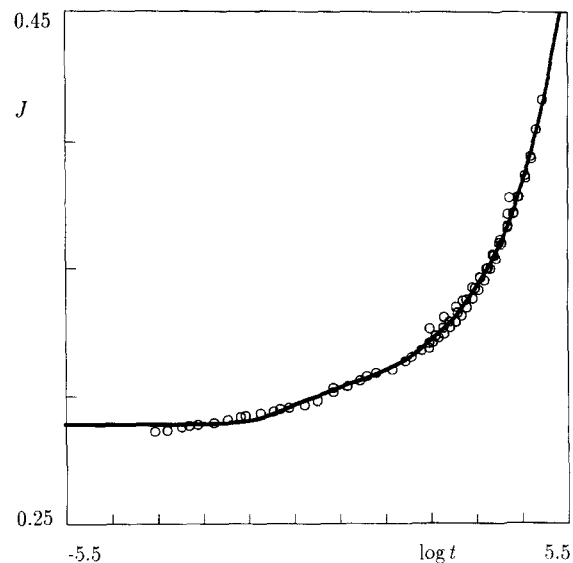


Figure 10 The short-term creep compliance J (GPa^{-1}) versus time t (s) [the master curve is reduced to $t_e^0 = 72$ (h)] for poly(vinyl chloride) Darvic quenched from 85 to 23°C. Circles, treatment of experimental data obtained by Read *et al.*⁹. The solid line represents their approximation by equation (54) and equation (57) with $\mu = 3.46$ (GPa) and

χ_m	γ_{m0} (s^{-1})
0.3907	0.000005
0.1076	0.000050
0.0660	0.000500
0.0370	0.005000
0.0194	0.050000
0.0233	0.500000
0.0266	5.000000

satisfy the ordinary differential equations

$$\frac{dP_m}{dt}(t) = \gamma_{m0}[Q(t) - P_m(t)], \quad P_m(0) = 0 \quad (59)$$

Equations (58) and (59) are integrated numerically to calculate the dependence $Q = Q(t)$, which, in turn, is approximated by the truncated Prony series

$$Q(t) = - \sum_{m=1}^M \eta_m [1 - \exp(-\gamma_{m0}t)] \quad (60)$$

The adjustable parameters η_m are found to ensure the best fit of the relaxation measure $Q(t)$.

Given M , b_k , η_m , and γ_{m0} , the material response in long-term creep tests is determined by the integral equation (51), where the functions $n_m(t)$ and $N_m(t, \tau)$ obey equation (15). We introduce the notation

$$\bar{N}_m(t) = \int_0^t N_m(t, \tau) d\tau, \quad \Psi_m(t) = \int_0^t N_m(t, \tau) J_{t_c}(\tau) d\tau \quad (61)$$

and present equation (51) in the form

$$\left\{ 1 - \sum_{m=1}^M \eta_m [1 - n_m(t) - \bar{N}_m(t)] \right\} J_{t_c}(t) = \mu^{-1} + \sum_{m=1}^M \eta_m \Psi_m(t) \quad (62)$$

where

$$J_{t_c}(t) = \frac{\epsilon_{t_c}(t)}{\sigma}$$

It follows from equations (15) and (61) that the function

$$\Phi_m(t) = n_m(t) + \bar{N}_m(t) - 1$$

satisfies the linear homogeneous differential equation

$$\frac{d\Phi_m}{dt}(t) = -\gamma_m(t)\Phi_m(t)$$

with the zero initial condition $\Phi_m(0) = 0$, which implies that

$$\Phi_m(t) = 0 \quad (63)$$

Combining equation (62) and (63), we find that

$$J_{t_e}(t) = \mu^{-1} + \sum_{m=1}^M \eta_m \Psi_m(t) \quad (64)$$

According to equation (15) and (61), the function $\Psi_m(t)$ is governed by the ordinary differential equations

$$\frac{d\Psi_m}{dt}(t) = -\gamma_m(t)[J_{t_e}(t) - \Psi_m(t)], \quad \Psi_m(0) = 0 \quad (65)$$

where the function $\gamma_m(t)$ is determined by equation (49).

We calculate the long-term creep compliance $J_{t_e}(t)$ by solving numerically equation (64) and (65), and compare the results of calculations with experimental data. Figure 11 demonstrates fair agreement between experimental data and numerical prediction, which means that the model may be used to describe the long-term response in aging polymers.

CONCLUDING REMARKS

A new model is derived to predict the long-term viscoelastic response in physically aging polymers. The model incorporates the concept of transient polymeric networks with free volume theory.

An aging viscoelastic medium is treated as a network of adaptive links (elastically active chains) which emerge (reformation of dangling chains) and break (snapping of ends of active chains from temporal junctions). It is assumed that M different kinds of adaptive links exist, which correspond to different characteristic lengths of the interaction between chains.

The balance equation (3) is developed for the numbers of links of various kinds. An explicit solution of this equation is derived for non-aging materials, which expresses the breakage functions in terms of the reformation rates. Based on equation (12), kinetic equations (15) are proposed for the numbers of adaptive links of various kinds. Coefficients in these equations (the reformation rates) are assumed to satisfy the superposition principle (equation (17)), where the shift factor a is a function of temperature and increment of the free volume fraction; see equation (30).

With reference to the experimental data for poly(vinyl chloride) and polycarbonate, simple kinetic equations (27) are suggested for the free volume fractions of adaptive links of various kinds, and a linear dependence (equation (32)) is proposed to express the relative shift factor $a_{r,2}$ in terms of the excess free volume fraction Δf . For isothermal loading, this dependence may be reduced to the linear function equation (48) with two adjustable parameters.

Based on the model of adaptive links, the constitutive equation (42) is derived for a linear viscoelastic medium subjected to aging. Adjustable parameters in the constitutive relationship are determined by fitting experimental data obtained in short-term creep and relaxation tests for polystyrene and poly(vinyl chloride). To validate the model, its prediction for long-term creep and relaxation tests is compared with experimental data. The results of a

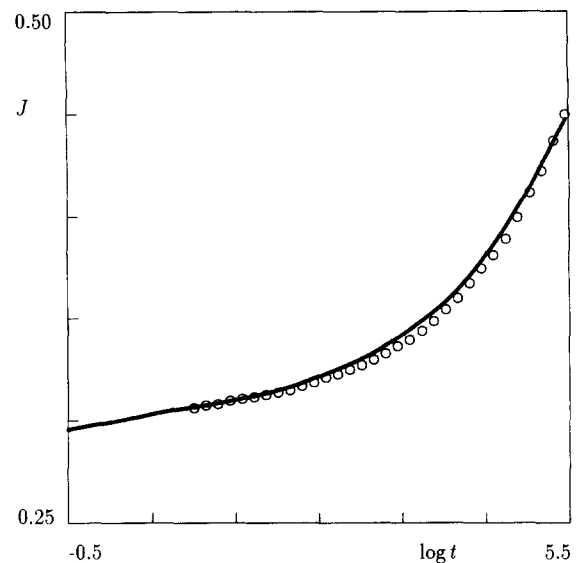


Figure 11 The long-term creep compliance J (GPa^{-1}) versus time t (s) for poly(vinyl chloride) Darvic quenched from 85 to 23°C. Circles, experimental data obtained by Read *et al.*⁹. The solid line represents the model prediction

numerical analysis demonstrate fair agreement with observations; see Figures 7 and 11, which may serve as a validation of the model.

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