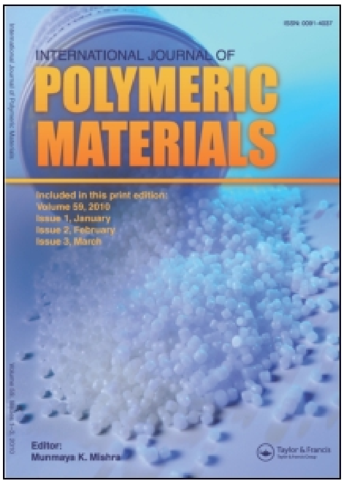

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

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Aleksey D. Drozdov[a]
[a] Institute for Industrial Mathematics, Beersheba, Israel

To cite this Article Drozdov, Aleksey D.(2001) 'The Trapping Concept in Nonlinear Viscoelasticity of Amorphous Glassy Polymers', International Journal of Polymeric Materials, 49: 3, 339 — 353
To link to this Article: DOI: 10.1080/00914030108039785
URL: http://dx.doi.org/10.1080/00914030108039785

Intern. J. Polymeric Mater., 2001, Vol. 49, pp. 339-353
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The Trapping Concept in Nonlinear Viscoelasticity of Amorphous Glassy Polymers

ALEKSEY D. DROZDOV

*Institute for Industrial Mathematics, 4 Hanachtom Street,
Beersheba 84311, Israel*

(Received 2 September 1999)

Nonlinear stress-strain relations are derived for the viscoelastic behavior of glassy polymers. An amorphous medium is treated as an ensemble of cooperatively rearranging regions (flow units). Any unit is thought of as a point in the phase space which hops (being thermally activated) to higher energy levels in its potential well on the energy landscape. The viscoelastic behavior of a polymer is modeled as a sequence of rearrangement events occurring at random times when relaxing regions reach (in hops) some liquid-like level. We assume that external loads affect the position of the liquid-like state with respect to the energy landscape, and the descent of the reference energy level is proportional to the average mechanical energy of a flow unit. This hypothesis is verified by comparison of observations for polycarbonate in tensile relaxation tests with results of numerical simulation. Fair agreement is demonstrated between experimental data and their predictions.

Keywords: Nonlinear viscoelasticity; Glassy polymers; Thermal activation

1. INTRODUCTION

The paper is concerned with the nonlinear viscoelastic behavior of amorphous glassy polymers at isothermal loading in the sub-yield region. This subject has attracted substantial attention in the past decade because of its applications in polymer engineering [1-19]. However, despite significant successes in the analysis of time-dependent response of amorphous media, it is difficult to mention a model that establishes plausible correlations between deformations at the micro-level and material properties at the macro-level [20]. This may be explained by the insufficient knowledge of the influence of mechanical factors on the local rearrangement of long chains.

Conventional concepts in nonlinear viscoelasticity of polymers are based on the time-stress and time-strain superposition principles [21] which presume that stresses (strains) accelerate the rearrangement process. The specific free volume [22, 23] and the specific configurational entropy [24] are traditionally employed as measures of the activation. In spite of numerous applications of this approach to fit experimental data [1, 2, 5, 8–11], its ability to correctly predict the viscoelastic response remains questionable, because it fails to describe the following phenomena revealed in mechanical tests on glassy polymers:

1. tensile and torsional relaxation curves at strains in the sub-yield region plotted in double logarithmic coordinates cannot be superposed with an acceptable accuracy by horizontal and vertical shifts [25, 26];
2. oscillation tests on stretched specimens demonstrate a pronounced decrease in the loss tangent with time when the samples are stretched with a constant rate of straining [27], as well as in creep and relaxation modes [25, 28, 29].

This implies that new constitutive equations should be developed which can predict the above observations. The characteristic feature of the model in search is that the rearrangement process is described by such a mechanical parameter that does not remain constant in tests with constant strains and stresses.

In this study we attempt to derive stress–strain relations in nonlinear viscoelasticity of polymers using the trapping concept [30–33]. In agreement with the theory of cooperative relaxation, an amorphous polymer is treated as an ensemble of mutually independent flow units. A unit is thought of as a globule consisting of scores of strands of long chains connected by attractive and repulsive forces between monomeric units and changing their positions simultaneously. The evidence in favor of this picture is provided by measurements of dielectric relaxation and the Kerr effect in glass-forming liquids [30, 34]. The characteristic length of a relaxing region in the vicinity of the glass transition temperature T_g amounts to several nanometers [35].

In the phase space, units are modeled as material points located at bottom levels of their potential wells. At random times, relaxing regions hop to higher energy levels being thermally activated, and, afterward, return to the initial positions. This scenario reflects the concept of ergodicity breaking [36], which states that below T_g flow units cannot change their traps.

With reference to the transition-state theory [37], we assume that some liquid-like (reference) state exists on the energy landscape, where flow units change their configurations. When a unit reaches the liquid-like energy level in a hop, stresses totally relax because of rearrangement of strands. When the hop is short of the reference state, the relaxing region lands in its potential well without changes. The viscoelastic behavior of an amorphous polymer is modeled as sequential rearrangement of relaxing regions.

The novelty of our approach is that the reference energy level is permitted to change its position with respect to the energy landscape. It is assumed that external loads cause a descent of the liquid-like level (compared to its position in a stress-free medium) which is proportional to the current average mechanical energy of a polymer. Based on this hypothesis, we fit (with a high level of accuracy) relaxation curves for polycarbonate at strains up to 7 percent, when standard methods of superposition fail to match observations.

The exposition is organized as follows. Section 2 deals with governing equations for rearrangement of flow units. Constitutive equations for amorphous glassy polymers are derived in Section 3. The stress–strain relations are applied to fit experimental data in Section 4. Some concluding remarks are formulated in Section 5.

2. KINETICS OF REARRANGEMENT OF FLOW UNITS

An amorphous polymer is treated as an ensemble of cooperatively rearranging regions with various energies. In the phase space, a region is modeled as a point located at the bottom level of its potential well. The depth of the potential well with respect to the reference state of a stress-free medium is determined by potential energy w. For definiteness, we set $w=0$ for the initial reference state and $w>0$ for an arbitrary flow unit.

Denote by Ξ_0 the (time-uniform) concentration of cages per unit mass of the bulk medium and by $\Xi(t, \tau, w)$ the current (at time t) concentration of traps with potential energy w which have rearranged for the last time before instant $\tau \leq t$. The function $\Xi(t, \tau, w)$ provides a detailed description of the rearrangement process: $\Xi(t, 0, w)$ is the current concentration of traps with potential energy w where rearrangement has not occurred; $\Xi(t, t, w)$ is the concentration of traps with energy w at time t; the quantity

$$\frac{\partial \Xi}{\partial \tau}(t, \tau, w)\bigg|_{t=\tau} d\tau$$

is the number of flow units in traps with energy w that reach the reference level within the interval $[\tau, \tau + d\tau]$; and the amount

$$\frac{\partial \Xi}{\partial \tau}(t, \tau, w) d\tau$$

is the number of these regions not rearranged within the interval $[\tau, t]$. The number of initial flow units in traps with energy w rearranged within the interval $[t, t + dt]$ reads

$$-\frac{\partial \Xi}{\partial t}(t, 0, w) dt,$$

and the number of relaxing regions in traps with energy w that have rearranged for the last time within the interval $[\tau, \tau + d\tau]$ before reaching the reference state within the interval $[t, t + dt]$ is given by

$$-\frac{\partial^2 \Xi}{\partial t \partial \tau}(t, \tau, w) dt d\tau.$$

Denote by $q(\omega)d\omega$ the probability for a flow unit to reach in an arbitrary hop the energy level that exceeds the bottom level of its well by a value located in the interval $[\omega, \omega + d\omega]$. Referring to the extreme value statistics [38], we set

$$q(\omega) = \alpha \exp(-\alpha \omega),$$

where α is a material constant. The probability to reach the reference state in a hop reads

$$Q(t,w) = \int_{w-\Omega(t)}^{\infty} q(\omega)d\omega = \exp[-\alpha(w - \Omega(t))],$$

where $\Omega(t)$ is the descent energy of the liquid-like level at time t with respect to its position in a stress-free medium. Assuming the average rate of hops Γ to be constant and multiplying Γ by the probability of reaching the liquid-like state in a hop $Q(t,w)$, we arrive at the analog of the Eyring formula [39] for the rate of rearrangement

$$P(t,w) = P_0(w)\exp[-\alpha\Omega(t)], \quad P_0(w) = \Gamma\exp(-\alpha\omega). \tag{1}$$

Equating the relative rates of rearrangement to the function P, we arrive at the differential equations

$$\begin{aligned} \frac{\partial\Xi}{\partial t}(t,0,w) &= -P(t,w)\Xi(t,0,w), \\ \frac{\partial^2\Xi}{\partial t\partial\tau}(t,\tau,w) &= -P(t,w)\frac{\partial\Xi}{\partial\tau}(t,\tau,w). \end{aligned} \tag{2}$$

The function $\Xi(t,\tau,w)$ is connected with the probability density of traps $p(w)$ by the formula

$$\Xi(t,t,w) = \Xi_0 p(w). \tag{3}$$

The number of relaxing regions (per unit mass) located in traps with potential energies lying in the interval $[w, w+dw]$ that rearrange per unit time equals

$$\Xi_0 P(t,w)p(w)dw.$$

Since the duration of a hop (a few picoseconds [34,40]) is small compared to the characteristic time of relaxation in the α-region, hops are thought of as instantaneous. Neglecting the duration of a hop, we find that the same number of flow units land in their traps per unit time,

$$\frac{\partial\Xi}{\partial\tau}(t,\tau,w)\bigg|_{t=\tau} = \Xi_0 P(\tau,w)p(w). \tag{4}$$

The solutions of Eq. (2) with initial conditions (3) and (4) read

$$\begin{aligned} \Xi(t,0,w) &= \Xi_0 p(w) \exp\left[-\int_0^t P(s,w)ds\right], \\ \frac{\partial \Xi}{\partial \tau}(t,\tau,w) &= \Xi_0 P(\tau,w)p(w) \exp\left[-\int_\tau^t P(s,w)ds\right]. \end{aligned} \tag{5}$$

3. STRESS-STRAIN RELATIONS

We study uniaxial deformation of a specimen when only one component ε of the strain tensor does not vanish. Uniaxial constitutive relations may be extended to three-dimensional loading by conventional methods [15].

Because a flow unit totally relaxes when it reaches the liquid-like state, its natural (stress-free) configuration coincides with the actual configuration of the bulk medium at the instant of rearrangement. The nominal strain in the relaxing region (the strain from its natural configuration to the actual configuration at time t) reads

$$\varepsilon_0(t,\tau) = \varepsilon(t) - \varepsilon(\tau),$$

where $\tau \leq t$ is the last instant when the region has rearranged. We assume that the mechanical energy of a flow unit U is independent of the depth of potential wells,

$$U = U(\varepsilon_0(t,\tau)),$$

where the function $U(\varepsilon)$ satisfies the conditions

$$U(0) = 0, \quad \frac{\partial U}{\partial \varepsilon}(0) = 0. \tag{6}$$

The specific mechanical energy (per unit mass) of initial flow units which have not rearranged during the interval $[0,t)$ is given by

$$U(\varepsilon(t)) \int_0^\infty \Xi(t,0,w)dw.$$

The specific mechanical energy of flow units rearranged within the interval $[\tau, \tau + d\tau]$ that have not returned to the liquid-like state until the current time t is calculated as

$$U(\varepsilon(t) - \varepsilon(\tau))d\tau \int_0^\infty \frac{\partial \Xi}{\partial \tau}(t, \tau, w)dw.$$

Summing these expressions and neglecting the energy of interaction between relaxing regions, we find the specific mechanical energy of an amorphous polymer

$$\Phi(t) = U(\varepsilon(t)) \int_0^\infty \Xi(t, 0, w)dw + \int_0^t U(\varepsilon(t) - \varepsilon(\tau))d\tau \int_0^\infty \frac{\partial \Xi}{\partial \tau}(t, \tau, w)dw. \tag{7}$$

At small strains, the stress σ is expressed in terms of the specific mechanical energy Φ by the formula

$$\sigma(t) = \rho \frac{\partial \Phi(t)}{\partial \varepsilon(t)},$$

where ρ is mass density in the stress-free state. Substitution of expressions (5) and (7) into this equality results in the stress–strain relation

$$\sigma(t) = V(\varepsilon(t)) \int_0^\infty p(w) \exp\left[-\int_0^t P(s, w)ds\right] dw + \int_0^t V(\varepsilon(t) - \varepsilon(\tau))d\tau \int_0^\infty P(\tau, w)p(w) \exp\left[-\int_\tau^t P(s, w)\right] dw, \tag{8}$$

where

$$V(\varepsilon) = \rho \Xi_0 \frac{dU}{d\varepsilon}(\varepsilon). \tag{9}$$

4. COMPARISON WITH EXPERIMENTS

For the standard relaxation test with

$$\varepsilon(t) = \begin{cases} 0, & t < 0, \\ \varepsilon, & t > 0, \end{cases}$$

Equations (5) to (8) imply that

$$\varphi(t) = U(\varepsilon)\int_0^\infty p(w)\exp\left[-P_0(w)\int_0^t \exp(-\alpha\Omega(s))ds\right]dw,$$
$$\sigma(t) = V(\varepsilon)\int_0^\infty p(w)\exp\left[-P_0(w)\int_0^t \exp(-\alpha\Omega(s))ds\right]dw, \tag{10}$$

where φ is the average mechanical energy of a trap.

According to the random energy model [40], the distribution of cages is described by the Gaussian formula

$$p(w) = \frac{1}{\sqrt{2\pi}\sum}\exp\left[-\frac{(w-W)^2}{2\sum^2}\right], \tag{11}$$

where W is the average depth of a potential well and $\sum$ is the standard deviation of energies of wells.

Our main hypothesis is that the descent energy of the liquid-like state Ω is proportional to the average mechanical energy φ,

$$\Omega(t) = A\varphi(t), \tag{12}$$

where A is an adjustable parameter. Combining Eqs. (1) and (10) to (12), we arrive at the nonlinear integral equation for the function $\Omega_0(t)=\alpha\Omega$,

$$\Omega_0(t) = U_0(\varepsilon)\int_0^\infty \exp\left[-\left(\frac{(z-W_*)^2}{2\sum_*^2}+\Gamma\exp(-z)\times\int_0^t \exp(-\Omega_0(s))ds\right)\right]dz, \tag{13}$$

where $z=\alpha w$, $W_*=\alpha W$, $\sum_*=\alpha\sum$ and

$$U_0(\varepsilon) = \frac{\alpha A U(\varepsilon)}{\sqrt{2\pi}\sum_*}.$$

It follows from Eqs. (1) and (10) that

$$E(t,\varepsilon) = \frac{E_0(\varepsilon)}{\sqrt{2\pi}\sum_*}\int_0^\infty \exp\left[-\left(\frac{(z-W_*)^2}{2\sum_*^2}+\Gamma\exp(-z)\times\int_0^t \exp(-\Omega_0(s))ds\right)\right]dz, \tag{14}$$

where $E(t, \varepsilon) = \sigma(t)/\varepsilon$ is the current Young modulus and

$$E_0(\varepsilon) = \frac{V(\varepsilon)}{\varepsilon}. \tag{15}$$

Given a strain ε, Eqs. (13) and (14) are determined by 5 adjustable parameters: the quantities W_* and $\sum_*$ determine the relaxation spectrum (the distribution of traps with various depths), the constant Γ is the rate of hops, and the amounts E_0 and U_0 characterize mechanical energies of individual flow units. It follows from the structure of Eqs. (13) and (14) that one of the quantities Γ and W_* may be chosen *a priori*, whereas the other is found by fitting observations. For definiteness, the value W_* is fixed.

We begin with observations in tensile relaxation tests for polycarbonate at the temperature $T = 50°\text{C}$. For a detailed description of experimental procedure, see Ref. [26]. First, we match a relaxation

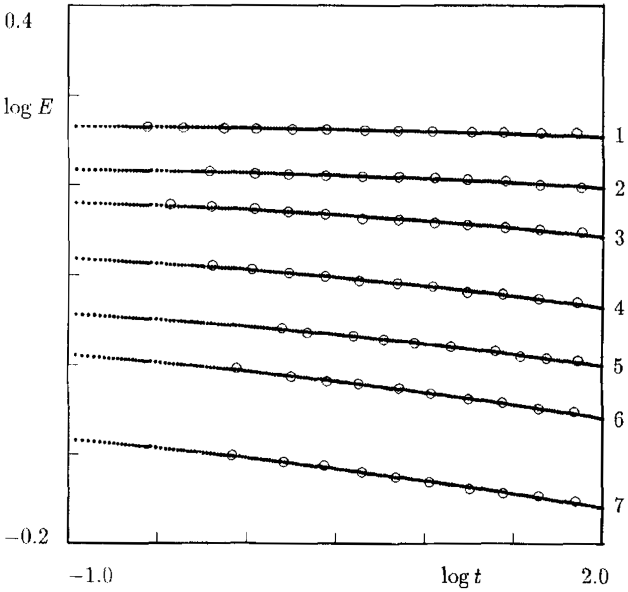

FIGURE 1 The Young modulus E GPa *versus* time t min for uniaxial extension of polycarbonate at $T = 50°\text{C}$. Circles: experimental data [26]. Solid lines: prediction of the model. Curve 1: $\varepsilon = 0.007$; curve 2: $\varepsilon = 0.020$; curve 3: $\varepsilon = 0.031$; curve 4: $\varepsilon = 0.042$; curve 5: $\varepsilon = 0.047$; curve 6: $\varepsilon = 0.052$; curve 7: $\varepsilon = 0.0625$.

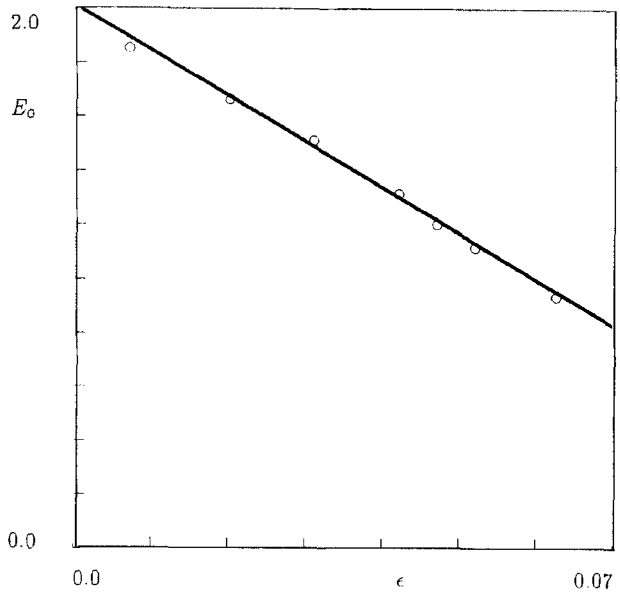

FIGURE 2 The initial Young modulus E_0 GPa *versus* strain ε for polycarbonate in tensile relaxation tests at $T = 50°C$. Circles: treatment of observations [26]. Solid line: approximation of experimental data by Eq. (16) with $C_0 = 2.01$ and $C_1 = 16.89$.

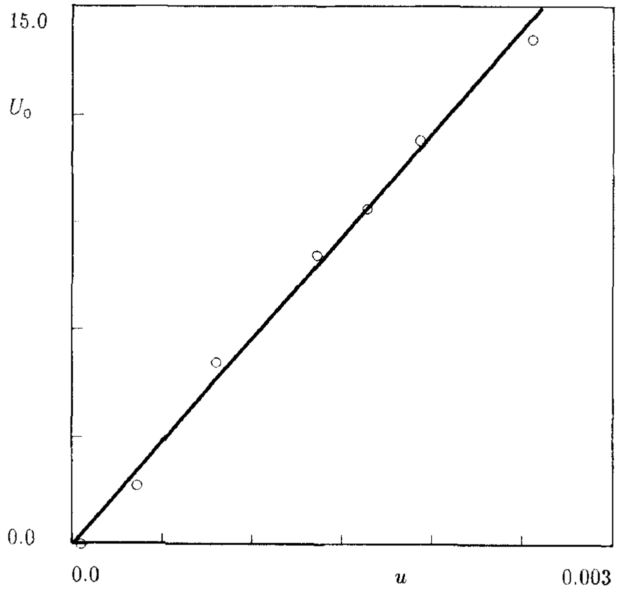

FIGURE 3 The dimensionless quantity U_0 *versus* the energy u GPa for polycarbonate in tensile relaxation tests at $T = 50°C$. Circles: treatment of observations [26]. Solid line: approximation of experimental data by Eq. (17) with $C = 5747.97$.

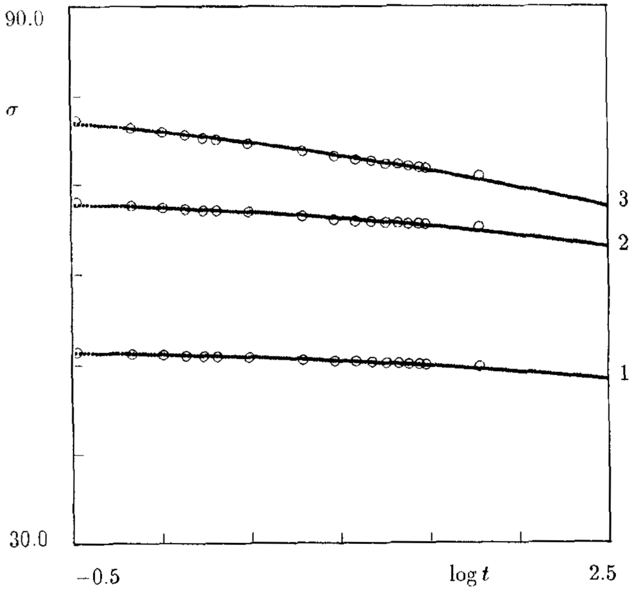

FIGURE 4 The stress σ MPa *versus* time t min for polycarbonate in tensile relaxation tests at $T=-24°C$. Circles: experimental data [25]. Solid lines: prediction of the model. Curve 1: $\varepsilon=0.0185$; curve 2: $\varepsilon=0.0320$; curve 3: $\varepsilon=0.0508$.

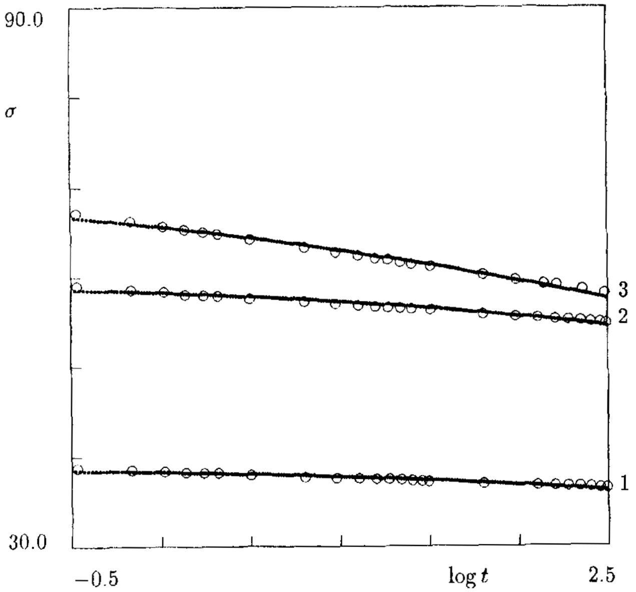

FIGURE 5 The stress σ MPa *versus* time t min for polycarbonate in tensile relaxation tests at $T=26°C$. Circles: experimental data [25]. Solid lines: prediction of the model. Curve 1: $\varepsilon=0.0185$; curve 2: $\varepsilon=0.0320$; curve 3: $\varepsilon=0.0508$.

curve measured in the region of linear viscoelasticity ($\varepsilon = 0.003$), where changes in the position of the reference energy level may be neglected ($\Omega_0 = 0$). The parameters Γ and $\sum_*$ are found from the condition of the best fit of experimental data. Afterward, we fix the parameters $\Gamma = 13.2\,\text{min}^{-1}$, $W_* = 24.0$ and $\sum_* = 8.46$, and determine the parameters $U_0(\varepsilon)$ and $E_0(\varepsilon)$ which ensure the best approximation of relaxation curves measured at various longitudinal strains ε. The quantity E_0 is found by the least-squares method, whereas the amount U_0 is detected using the steepest-descent procedure. Observations are plotted together with results of numerical simulations in Figure 1 which demonstrates that Eq. (14) correctly predicts experimental data.

According to Figure 2, the dependence $E_0(\varepsilon)$ is fairly well approximated by the linear function

$$E_0(\varepsilon) = C_0 - C_1\varepsilon \tag{16}$$

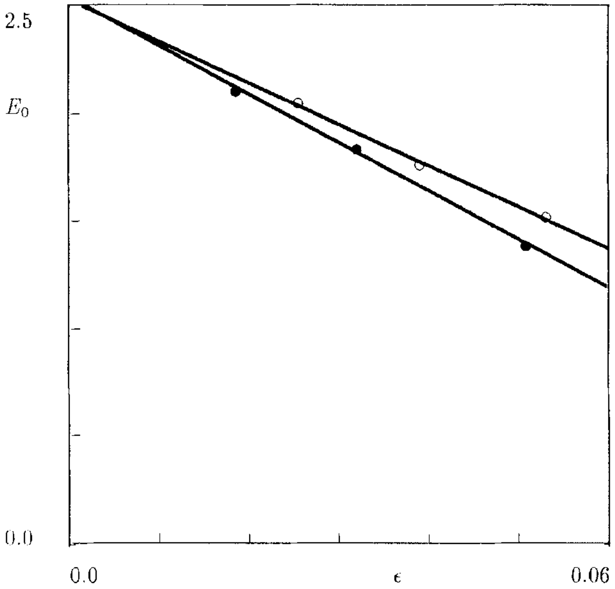

FIGURE 6 The initial Young modulus E_0 GPa *versus* strain ε for polycarbonate in tensile relaxation tests at temperature T°C. Circles: treatment of observations [25]. Solid line: approximation of experimental data by Eq. (16). Curve 1: $T = -24$, $C_0 = 2.52$ and $C_1 = 19.24$, curve 2: $T = 26$, $C_0 = 2.54$, $C_1 = 22.48$.

with adjustable parameters C_0 and C_1. It follows from Eqs. (6), (9), (15) and (16) that

$$U_0(\varepsilon) = Cu(\varepsilon), \quad u(\varepsilon) = \frac{1}{2}C_0\varepsilon^2 - \frac{1}{3}C_1\varepsilon^3, \tag{17}$$

where C is a constant. Figure 3 evidences that Eq. (17) ensures excellent agreement with observations.

To illustrate that the model adequately describes the nonlinear viscoelastic response of polycarbonate at other temperatures, we repeat the calculations using experimental data adopted from Ref. [25]. Figures 4 and 5 show excellent correspondence between measurements and results of numerical simulation with $\Gamma = 0.16\,\text{min}^{-1}$, $W_* = 20.0$ and $\sum_* = 7.9$. Figures 6 and 7 demonstrate that Eqs. (16) and (17) correctly predict mechanical energies of flow units.

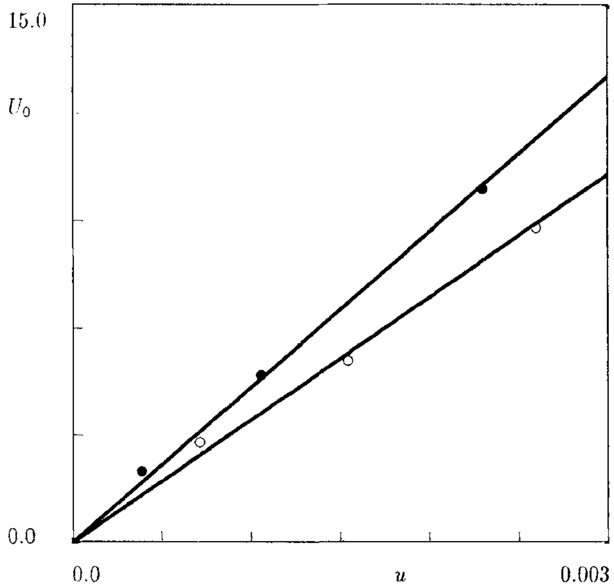

FIGURE 7 The dimensionless parameter U_0 *versus* the energy u GPa for polycarbonate in tensile relaxation tests at temperature T°C. Circles: treatment of observations [25]. Solid line: approximation of experimental data by Eq. (17). Curve 1: $T = -24$, $C = 3441.04$, curve 2: $T = 26$, $C = 4359.36$.

5. CONCLUSIONS

Constitutive equations have been derived for the nonlinear viscoelastic response of amorphous glassy polymers at isothermal loading. A disordered medium is treated as an ensemble of flow units trapped in cages. In the phase space, relaxing regions are located at the bottom levels of their potential wells, and they hop (at random times) to higher energy levels because of thermal excitations. Rearrangement of a flow unit occurs when it reaches the liquid-like state in a hop.

Unlike conventional models, we suppose that the position of the liquid-like level (with respect to the energy landscape) is not fixed, and it can move being driven by mechanical factors. The energy of descent of the reference level (compared to its position in a stress-free polymer) is proportional to the average mechanical energy per relaxing region.

Time-dependent response of an amorphous polymer at uniaxial loading is described by two nonlinear integral equations for the current stress σ and the current energy of a flow unit φ. An important advantage of Eqs. (13) and (14) is that they contain a small number of adjustable parameters (compared to conventional models in nonlinear viscoelasticity) which can be easily found by fitting observations.

The stress–strain relations are simplified for the standard relaxation test, and adjustable parameters are determined by matching relaxation curves for polycarbonate in a wide range of temperatures. It is demonstrated that the model correctly predicts experimental data in static tests with various strains ranging from the region of linear viscoelasticity to the sub-yield domain. Temperature rather weakly affects parameters of the model: the most pronounced growth with T (about by twice) is observed in the coefficient C which characterizes the effect of mechanical factors on the position of the reference level. This means that coupling between Eqs. (13) and (14) may become essentially important in the sub-T_g region.

Acknowledgement

The work was supported by the Israeli Ministry of Science through grants 9641-1-96 and 1202-1-98.

References

[1] Tieghi, G., Levi, M., Fallini, A. and Danusso, F. (1991). *Polymer*, **32**, 39.
[2] Losi, G. U. and Knauss, W. G. (1992). *Polym. Eng. Sci.*, **32**, 542.
[3] Wineman, A. S. and Waldron, W. K. (1993). *Polym. Eng. Sci.*, **33**, 1217.
[4] Buckley, C. P. and Jones, D. C. (1995). *Polymer*, **36**, 3301.
[5] Chengalva, M. K., Kenner, V. H. and Popelar, C. H. (1995). *Int. J. Solids Structures*, **32**, 847.
[6] Hasan, O. A. and Boyce, M. C. (1995). *Polym. Eng. Sci.*, **35**, 331.
[7] Waldron, W. K., McKenna, G. B. and Santore, M. M. (1995). *J. Rheol.*, **39**, 471.
[8] Mariani, P., Frassine, R., Rink, M. and Pavan, A. (1996). *Polym. Eng. Sci.*, **36**, 2750.
[9] Rand, J. L., Henderson, J. K. and Grant, D. A. (1996). *Polym. Eng. Sci.*, **36**, 1058.
[10] Strganac, T. W. and Golden, H. J. (1996). *Int. J. Solids Structures*, **33**, 4561.
[11] Tervoort, T. A., Klompen, E. T. J. and Govaert, L. E. (1996). *J. Rheol.*, **40**, 779.
[12] Colucci, D. M., O'Connell, P. A. and McKenna, G. B. (1997). *Polym. Eng. Sci.*, **37**, 1469.
[13] Simon, P. P. and Ploehn, H. J. (1997). *J. Rheol.*, **41**, 641.
[14] Zhang, C. and Moore, I. D. (1997). *Polym. Eng. Sci.*, **37**, 404.
[15] Drozdov, A. D., *Mechanics of Viscoelastic Solids* (Wiley, Chichester, 1998).
[16] Hassani, S., Alaoui Soulimani, A. and Ehrlacher, A. (1998). *Eur. J. Mech. A/Solids*, **17**, 567.
[17] Reese, S. and Govindjee, S. (1998). *Int. J. Solids Structures*, **35**, 3455.
[18] Wineman, A., van Dyke, T. and Shi, S. (1998). *Int. J. Mech. Sci.*, **40**, 1295.
[19] Jung, G.-D. and Youn, S.-K. (1999). *Int. J. Solids Structures*, **36**, 3755.
[20] Xiao, C., Jho, J. Y. and Yee, A. F. (1994). *Macromolecules*, **27**, 2761.
[21] Schapery, R. A. (1969). *Polym. Eng. Sci.*, **9**, 295.
[22] Doolittle, A. K. (1951). *J. Appl. Phys.*, **22**, 1471.
[23] Cohen, M. H. and Grest, G. S. (1979). *Phys. Rev. B*, **20**, 1077.
[24] Adam, G. and Gibbs, J. H. (1965). *J. Chem. Phys.*, **43**, 139.
[25] Litt, M. H. and Torp, S. (1973). *J. Appl. Phys.*, **44**, 4282.
[26] Ricco, T. and Smith, T. L. (1985). *Polymer*, **26**, 1979.
[27] Yoshioka, S., Usada, H. and Nanzai, Y. (1994). *J. Non-Cryst. Solids*, **172–174**, 765.
[28] Kolman, H. J., Ard, K. and Beatty, C. L. (1982). *Polym. Eng. Sci.*, **22**, 950.
[29] Othmezouri-Decerf, J. (1988). *Polymer*, **29**, 641.
[30] Dyre, J. C. (1987). *Phys. Rev. Lett.*, **58**, 792.
[31] Bouchaud, J. P. (1992). *J. Phys. I France*, **2**, 1705.
[32] Dyre, J. C. (1995). *Phys. Rev. B*, **51**, 12276.
[33] Monthus, C. and Bouchaud, J.-P. (1996). *J. Phys. A*, **29**, 3847.
[34] Dyre, J. C. (1999). *Phys. Rev. E*, **59**, 2458.
[35] Rizos, A. K. and Ngai, K. L. (1999). *Phys. Rev. E*, **59**, 612.
[36] Palmers, R. G. (1982). *Adv. Phys.*, **31**, 669.
[37] Goldstein, M. (1969). *J. Chem. Phys.*, **51**, 3728.
[38] Bouchaud, J.-P. and Mezard, M. (1997). *J. Phys. A*, **30**, 7997.
[39] Eyring, H. (1936). *J. Chem. Phys.*, **4**, 283.
[40] Richert, R. and Bässler, H. (1990). *J. Phys.: Cond. Mat.*, **2**, 2273.