The effects of temperature and molecular weight on the mechanical response and strength of elastomers

Aleksey D. Drozdov

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

Summary

Constitutive equations are derived for the mechanical behavior of rubbery polymers at finite strains. The model is based on the concept of rigid-rod networks, where breakage of chains is treated as bond scission. Adjustable parameters in the stress-strain relations are found by fitting observations in tensile tests for ethylene-octene copolymers. It is revealed that the constitutive equations correctly describe stress-strain curves up to the break points. Young's modulus and the critical strength per bond monotonically decrease with temperature and increase with molecular weight.

Introduction

This study deals with the isothermal mechanical behavior and ultimate strength of elastomers. Modeling the viscoelastic response and fracture of rubbery polymers has attracted substantial attention in the past half a century, which may be explained by a wide range of industrial applications of rubbers (1-3). Despite a number of studies concerned with either of these two subjects separately, it is difficult to mention a theory that establishes correlations between the stress-strain response and failure at the micro-level. A gap between these areas may be ascribed to the difference in basic concepts employed in the analysis of constitutive equations, on the one hand, and fracture of polymers, on the other. Conventional theories of rubber elasticity are grounded on the hypothesis that macromolecules are composed of so large numbers of strands that the mechanical energy of a chain is negligible compared to its configurational entropy. On the contrary, traditional approaches in fracture mechanics affiliate the breakage point with an instant when the essential work (4) (associated with the strain energy of chains) reaches some critical value (5-7).

This note concentrates on a correspondence between the mechanical response observed in tensile tests and the elongation to break for linear polymers. A polymer is treated as a network of rigid-rod chains whose configurational entropies are disregarded compared to their mechanical energies. The concept of rigid-rod networks was suggested in (8-11). This approach is applicable when $\mu \gg k_B T N$, where μ is the rigidity per bond, T is the absolute temperature, N is the average number of strands in a chain and k_B is Boltzmann's constant (10).

The following hypotheses are introduced:

1. A chain is treated as an ensemble of rigid (inextensible) rods connected in sequence and linked by bonds (10).

2. Two possible conformations are ascribed to a bond: flexed (*trans*) and extended (*cis*) (12).

3. In the equilibrium stress-free state, all bonds are in the flexed conformation. Under straining, some bonds change their conformations with the rate which is determined by the laws of thermodynamics.

4. The mechanical energy of a chain equals the sum of the strain energies of bonds with the flexed conformation (which are treated as linear elastic solids).

Conventional theories for fracture of rubbery polymers explain this phenomenon by uncoiling of long chains, their pullout (slippage of junctions with respect to the bulk material), bond scission (5,13), as well as by the growth of voids and formation of crosslink density gradients (14). With reference to observations demonstrating a substantial increase in the number of free radicals in the sub-fracture region (15,16), we postulate that bond scission is the main mechanism for failure of elastomers (13). By analogy with (5), slippage of junctions is disregarded, which is tantamount to the affinity hypothesis for deformation of polymeric networks. Pullout of chains and friction between them are neglected because these processes are important only in the close vicinity of crack fronts (17) and interfaces in polymeric blends (18). Uncoiling of chains is taken into account implicitly by means of a parameter η which characterizes end-to-end elongation of a chain induced by transition of a bond from its flexed to extended conformation. We concentrate on the catastrophic regime of fracture [when breakage of chains results in the formation of a crack percolating a specimen (19)] and assume that failure occurs when the strain per bond reaches its critical value Δ. This hypothesis may be treated as the deterministic version of the fiber bundle model (20,21). The critical strength per bond is defined as

$$\Sigma = \frac{\mu\Delta}{M_e},\tag{1}$$

where M_e is the average molecular weight between entanglements.

The effects of crosslink density and temperature on the ultimate strength of rubbery polymers have been recently studied in experimental works which concluded in rather controversial results. For example, Refs. (22,23) demonstrate that the fracture energy decreases with crosslink density, Ref. (24) reveals that the tensile strength increases with the number of crosslinks, whereas Refs. (5,6) show that toughness is a nonmonotonic function of the crosslink density with a maximum point. As another example, we refer to Refs. (6,25) which demonstrate that the ultimate strength decreases with temperature, and to Ref. (26) which reveals a nonmonotonic dependence of strength on temperature (experimental data are replotted in Fig. 1). These contradictions may be ascribed to different procedures of measurement for the ultimate strength, on the one hand, and to the fact that the conventional parameters explicitly associated with failure (elongation to break, maximum stress, toughness) are oversimplified characteristics of the fracture process, on the other.

We aim (i) to develop a molecular model for the mechanical response and fracture of elastomers, where rupture of a chain occurs when the strain per bond reaches its ultimate value Δ, (ii) to find adjustable parameters in the constitutive equations by fitting observations depicted in Fig. 1 and (iii) to demonstrate that the ultimate strength Σ monotonically changes with temperature and molecular weight M_w.

Deformation of a long chain

A linear polymer is thought of as a network of rigid-rod chains connected to permanent junctions (chemical crosslinks and entanglements). With reference to the Kratky-Porod model (11), a chain is treated as an aggregate consisting of $N + 1$ identical inextensible strands linked in sequel. A bond bridging two neighboring strands is
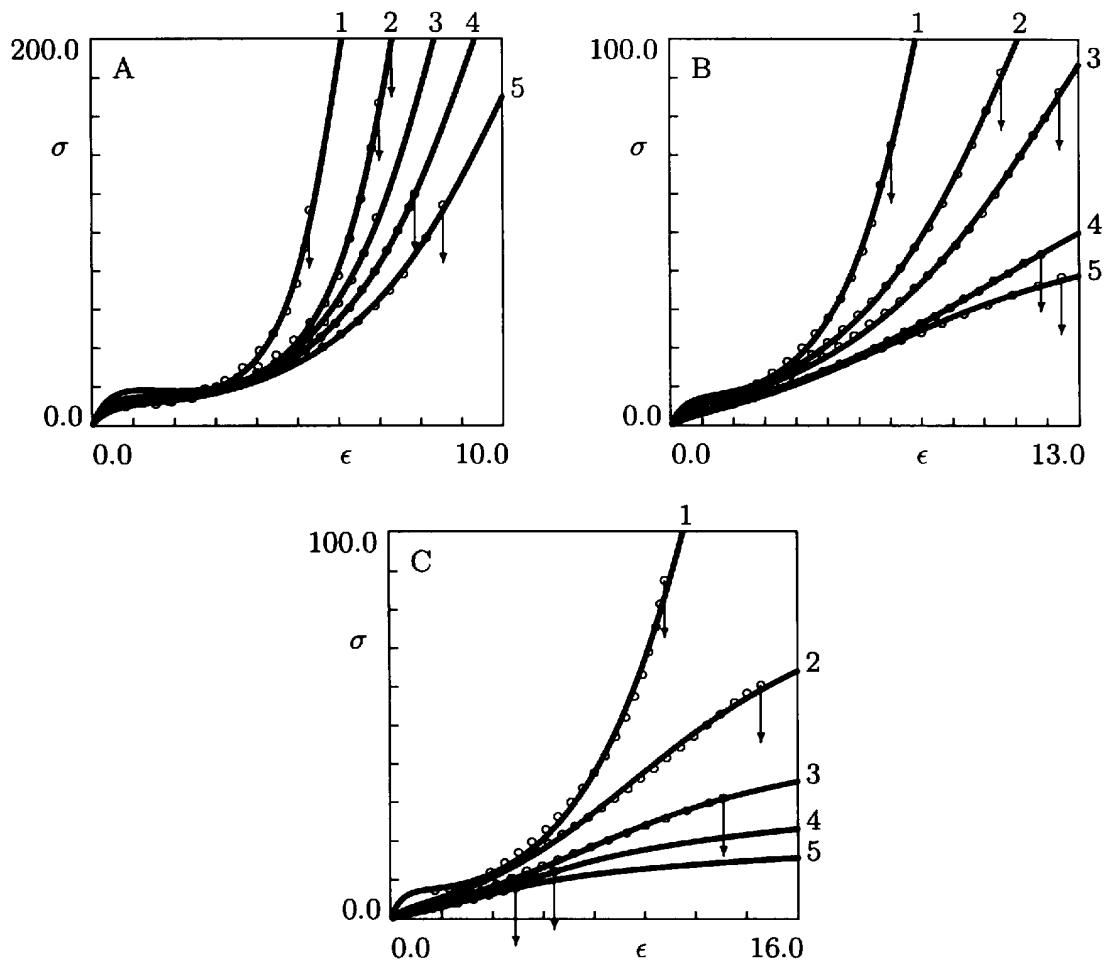
Figure 1: The true stress σ MPa versus the engineering strain ϵ for ethylene-octene copolymers CGCT87 with various molecular weights, M_w, in a tensile test with the strain rate $\dot{\epsilon}_0 = 1.0$ min^{-1} at $T = 0$ (A), $T = 25$ °C (B) and $T = 40$ °C (C). Circles: experimental data; vectors denote the breakage points (26). Solid lines: results of numerical simulation. Curve 1: $M_w = 13.17 \times 10^4$; curve 2: $M_w = 8.17 \times 10^4$; curve 3: $M_w = 6.86 \times 10^4$; curve 4: $M_w = 5.23 \times 10^4$; curve 5: $M_w = 4.02 \times 10^4$

characterized by one of the two stable conformations: flexed and extended. In the stress-free state the angle between two neighboring strands linked by a bond with the flexed conformation equals $\theta \in (0, \pi)$ (the same for all bonds) and that for a bond with the extended conformation is π [see Fig. 1 in Ref. (10)]. In thermal equilibrium before deformation all bonds are in the flexed conformation. Mechanical loading activates chains, which results in changes in conformations of some bonds. The numbers of bonds with flexed and extended conformations, N_f and N_e, obey the balance law $N_f + N_e = N$. Introducing the ratio, n, of bonds with the extended conformation to the total number of bonds, $n = N_e/N$, we find that

$$N_f = N(1 - n), \qquad N_e = Nn. \tag{2}$$

In a deformed state the angle between strands linked by a bond with the flexed conformation alters, whereas for a bond with the extended conformation (modeled as two rigid rods directed along a straight line) this angle remains unchanged. The strain, e, from the stress-free state of a chain to its deformed state equals the sum of

strains for bonds with the flexed conformation, $e = N_f e_f$, which implies that

$$e_f = \frac{e}{N(1-n)}.$$ (3)

Bonds with flexed conformations are modeled as linear elastic solids with the mechanical energy $\frac{1}{2}\mu e_f^2$, whereas the strain energy of bonds with the extended conformation vanishes. The mechanical energy of a chain, w, equals the sum of the mechanical energies for individual bonds. It follows from Eqs. (2) and (3) that

$$w(e) = \frac{\mu e^2}{2N(1-n)}.$$ (4)

To express the strain for a chain, e, in terms of the macro-strain tensor for the network, $\hat{\epsilon}$, we consider a chain which has a small end-to-end length δ and which is directed along the unit guiding vector $\bar{l}$ in the stress-free state. The end-to-end vectors for the chain in the reference state, $\bar{R}_0$, and in the deformed state at time $t \geq 0$, $\bar{R}(t)$, are given by (27)

$$\bar{R}_0 = \delta\bar{l}, \qquad \bar{R}(t) = \delta\bar{l} \cdot \bar{\nabla}_0\bar{r}(t) = [\bar{\nabla}_0\bar{r}(t)]^\top \cdot \delta\bar{l},$$ (5)

where $\bar{r}$ is the radius vector of a point in the deformed state, $\bar{\nabla}_0$ is the gradient operator in the stress-free state, the dot stands for inner product and $\top$ denotes transpose. The end-to-end length of the chain, ds, reads $ds^2 = \bar{R} \cdot \bar{R}$, which together with Eq. (5) implies that $ds_0 = \delta$ and $ds(t, \bar{l}) = \delta [\bar{l} \cdot \hat{C}(t) \cdot \bar{l}]^{1/2}$, where $\hat{C}(t) = \bar{\nabla}_0\bar{r}(t) \cdot [\bar{\nabla}_0\bar{r}(t)]^\top$ is the Cauchy deformation tensor for transition from the stress-free state of the network to its deformed state at time t. The extension ratio $\lambda(t, \bar{l})$ is defined as the ratio of the current end-to-end length, $ds(t, \bar{l})$, to that of the chain in its "activated" stress-free state, $ds°(t, \bar{l})$. The latter state is defined as a state of the chain which is suddenly unloaded, but for which the numbers of bonds with various conformations coincide with their current values, $N_f(t)$ and $N_e(t)$. It differs from the equilibrium stress-free state where the numbers of bonds with the flexed and extended conformations equal $N_f = N$ and $N_e = 0$. The difference between the end-to-end lengths of a chain in the activated state, $ds°(t, \bar{l})$, and in the equilibrium state, ds_0, determines the end-to-end elongation driven by transition of bonds from the flexed to extended conformations. We assume the transformation-induced end-to-end elongation to be proportional to the number of bonds acquiring the extended conformations, $ds°(t, \bar{l}) = \delta + Nn(t, \bar{l})\delta_0$, where δ_0 is an increment of the end-to-end length driven by an individual transition. It follows from these equalities that the Hencky strain for a chain, $e = \ln \lambda$, reads ($\eta = N\delta_0/\delta$)

$$e(t, \bar{l}) = \ln \frac{ds(t, \bar{l})}{ds°(t, \bar{l})} = \frac{1}{2}\ln[\bar{l} \cdot \hat{C}(t) \cdot \bar{l}] - \ln[1 + \eta n(t, \bar{l})].$$ (6)

Strain energy density of a network

We adopt the conventional assumption that the excluded-volume effect and other multi-chain effects are screened for an individual chain by surrounding macromolecules. This implies that the energy of interaction between chains may be neglected (under the hypothesis of incompressibility) and the mechanical energy of the network equals the sum of the mechanical energies for individual chains. Assuming the distribution of chains with guiding vectors $\bar{l}$ to be isotropic, we multiply the number of chains (per unit mass) with guiding vector $\bar{l}$ by their mechanical energy, w, sum the results for various guiding vectors, $\bar{l}$, and find the mechanical energy of the network

$$W(t) = \frac{\mu\Xi}{8\pi N} \int_0^{2\pi} d\varphi \int_0^\pi \frac{e^2(t, \vartheta, \varphi)}{1 - n(t, \vartheta, \varphi)} \sin\vartheta d\vartheta,$$ (7)

where ϑ and φ are Euler's angles which determine the position of the unit vector $\bar{l}$ and Ξ is the number of chains per unit mass. Differentiation of Eq. (7) with respect to time results in the formulas (simple algebra is omitted)

$$\frac{dW}{dt} = \hat{\Upsilon} : \hat{D} - J,$$

$$\hat{\Upsilon}(t) = \frac{\mu\Xi}{4\pi N} \int_0^{2\pi} d\varphi \int_0^\pi \frac{e(t,\vartheta,\varphi)}{1 - n(t,\vartheta,\varphi)} \frac{\hat{F}(t,\vartheta,\varphi)}{\bar{l} \cdot \hat{C}(t) \cdot \bar{l}} \sin\vartheta d\vartheta,$$

$$J(t) = \frac{\mu\Xi}{8\pi N} \int_0^{2\pi} d\varphi \int_0^\pi \frac{H(t,\vartheta,\varphi)}{[1 - n(t,\vartheta,\varphi)]^2} \frac{\partial n}{\partial t}(t,\vartheta,\varphi) \sin\vartheta d\vartheta$$

$$H(t,\vartheta,\varphi) = e(t,\vartheta,\varphi)\left\{ \frac{2\eta[1 - n(t,\vartheta,\varphi)]}{1 + \eta n(t,\vartheta,\varphi)} - e(t,\vartheta,\varphi) \right\}, \qquad (8)$$

where $\hat{D}(t)$ is the rate-of-strain tensor for the network, $\hat{F}(t, \bar{l}) = [\bar{\nabla}_0\bar{r}(t)]^\mathsf{T} \cdot (\bar{l} \otimes \bar{l}) \cdot \bar{\nabla}_0\bar{r}(t)$ is the generalized Finger tensor, the colon stands for convolution and $\otimes$ denotes tensor product.

Constitutive equations

Observations evidence that the temperature increment at straining is rather small, which implies that temperature T remains close to its reference value T_0. This means that the effect of temperature on material parameters, as well as thermal expansion of the network may be disregarded. For affine deformation of an incompressible network, the Clausius-Duhem inequality reads (28)

$$T\frac{dQ}{dt} = -S\frac{dT}{dt} - \frac{d\Psi}{dt} + \frac{1}{\rho}\left(\hat{\sigma}_d : \hat{D} - \frac{1}{T}\bar{q} \cdot \bar{\nabla}T\right) \geq 0. \qquad (9)$$

where ρ is mass density, q is the heat flux vector, $\hat{\sigma}_d$ is the deviatoric component of the Cauchy stress tensor $\hat{\sigma}$, Ψ is the free (Helmholtz) energy, S is the entropy and Q is the entropy production per unit mass. The free energy is given by

$$\Psi = \Psi_0 + (c - S_0)(T - T_0) - cT\ln\frac{T}{T_0} + W, \qquad (10)$$

where S_0 and ψ_0 are the entropy and the free energy in the equilibrium stress-free state at the reference temperature T_0 and c is the specific heat. The second and third terms on the right-hand side of Eq. (10) characterize the energy of thermal motion. Substitution of Eqs. (8) and (10) into Eq. (9) yields

$$T\frac{dQ}{dt} = \left(\frac{\hat{\sigma}_d}{\rho} - \hat{\Upsilon}\right) : \hat{D} - \left(S - S_0 - c\ln\frac{T}{T_0}\right)\frac{dT}{dt} + J - \frac{1}{\rho T}\bar{q} \cdot \bar{\nabla}T \geq 0. \qquad (11)$$

Applying the conventional reasoning (28) to Eq. (11), we find that the expressions in braces vanishes, which results in the formula for the Cauchy stress tensor

$$\hat{\sigma}(t) = -P(t)\hat{I} + G[\bar{\nabla}_0\bar{r}(t)]^\mathsf{T} \cdot \int_0^{2\pi} d\varphi \int_0^\pi \frac{e(t,\vartheta,\varphi)}{1 - n(t,\vartheta,\varphi)} \frac{\bar{l} \otimes \bar{l}}{\bar{l} \cdot \hat{C}(t) \cdot \bar{l}} \sin\vartheta d\vartheta \cdot \bar{\nabla}_0\bar{r}(t), \quad (12)$$

where $P(t)$ is pressure and $G = \rho\mu\Xi/(4\pi N)$. It follows from Eqs. (8) and (11) that the rate of the entropy production is nonnegative for an arbitrary loading program, provided that (i) the heat flux vector $\bar{q}$ obeys the Fourier law $\bar{q} = -\kappa\bar{\nabla}T$ with a positive thermal diffusivity κ and (ii) the function $n(t, \vartheta, \varphi)$ satisfies the kinetic equation

$$\frac{\partial n}{\partial t}(t,\vartheta,\varphi) = \alpha e(t,\vartheta,\varphi)\left\{ \frac{2\eta[1 - n(t,\vartheta,\varphi)]}{1 + \eta n(t,\vartheta,\varphi)} - e(t,\vartheta,\varphi) \right\}, \qquad n(0,\vartheta,\varphi) = 0, \quad (13)$$

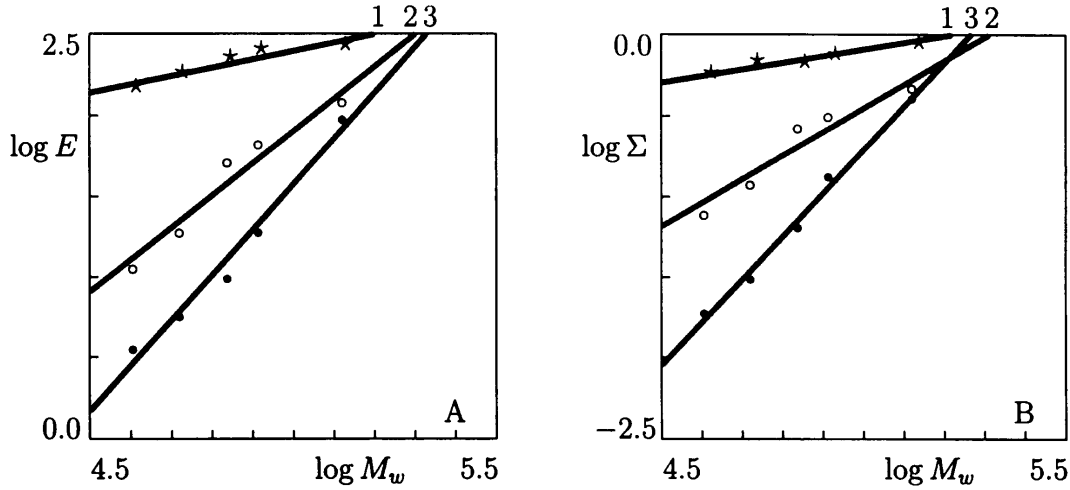where α is an adjustable parameter.

Figure 2: Young's modulus E MPa (A) and the ultimate strength per bond Σ (m/s)^2 (B) versus molecular weight M_w g/mol for ethylene-octene copolymer CGCT87 at $T = 0$ (stars), $T = 25$ (unfilled circles) and $T = 40$ °C (filled circles). Symbols: treatment of observations (26). Solid lines: approximation of the experimental data by the functions $\log E = E_0 + E_1 \log M_w$ and $\log \Sigma = \Sigma_0 + \Sigma_1 \log M_w$. A: Curve 1: $E_0 = -0.17$, $E_1 = 0.51$; curve 2: $E_0 = -8.03$, $E_1 = 1.99$; curve 3: $E_0 = -12.51$, $E_1 = 2.82$. B: Curve 1: $\Sigma_0 = -2.14$, $\Sigma_1 = 0.41$; curve 2: $\Sigma_0 = -7.75$, $\Sigma_1 = 1.46$; curve 3: $\Sigma_0 = -14.08$, $\Sigma_1 = 2.67$

Uniaxial tension of a specimen

At uniaxial extension of an incompressible specimen, Cartesian coordinates in the actual state, x_i, are expressed in terms of the Cartesian coordinates in the stress-free state, X_i, by the formulas

$$x_1 = k(t)X_1, \qquad x_2 = k^{-\frac{1}{2}}(t)X_2, \qquad x_3 = k^{-\frac{1}{2}}(t)X_3,$$

where $k = k(t)$ is the extension ratio. Bearing in mind that the functions $n = n(t, \vartheta)$ and $e = e(t, \vartheta)$ are independent of φ, we calculate the integral over φ in Eq. (12) explicitly, introduce the notation $z = \cos \vartheta$, $\tilde{e}(t, z) = e(t, \vartheta)$, $\tilde{n}(t, z) = n(t, \vartheta)$, and find the longitudinal stress

$$\sigma(t) = E \int_0^1 \frac{2k^2(t)z^2 - k^{-1}(t)(1 - z^2)}{k^2(t)z^2 + k^{-1}(t)(1 - z^2)} \frac{\tilde{e}(t, z)}{1 - \tilde{n}(t, z)} dz, \qquad E = \frac{\rho \mu \Xi}{2N}. \tag{14}$$

It follows from Eq. (6) that

$$\tilde{e}(t, z) = \ln \frac{[k^2(t)z^2 + k^{-1}(t)(1 - z^2)]^{\frac{1}{2}}}{1 + \eta \tilde{n}(t, z)}. \tag{15}$$

For a tensile test with a constant rate of engineering strain $\dot{\epsilon}_0$, $k(t) = 1 + \dot{\epsilon}_0 t$, Eq. (13) reads ($a = \alpha/\dot{\epsilon}_0$)

$$\frac{\partial \tilde{n}}{\partial k} = a\Big[\frac{2\eta(1 - \tilde{n})}{1 + \eta \tilde{n}} - \tilde{e}\Big]\tilde{e}, \qquad \tilde{n}(1, z) = 0. \tag{16}$$

Validation of the model

Equations (14) to (16) are determined by three adjustable parameters, E, a and η, which are found by fitting stress-strain curves for ethylene-octene copolymer CGCT87 (26). The parameters a and η are determined by the steepest-descent procedure and E
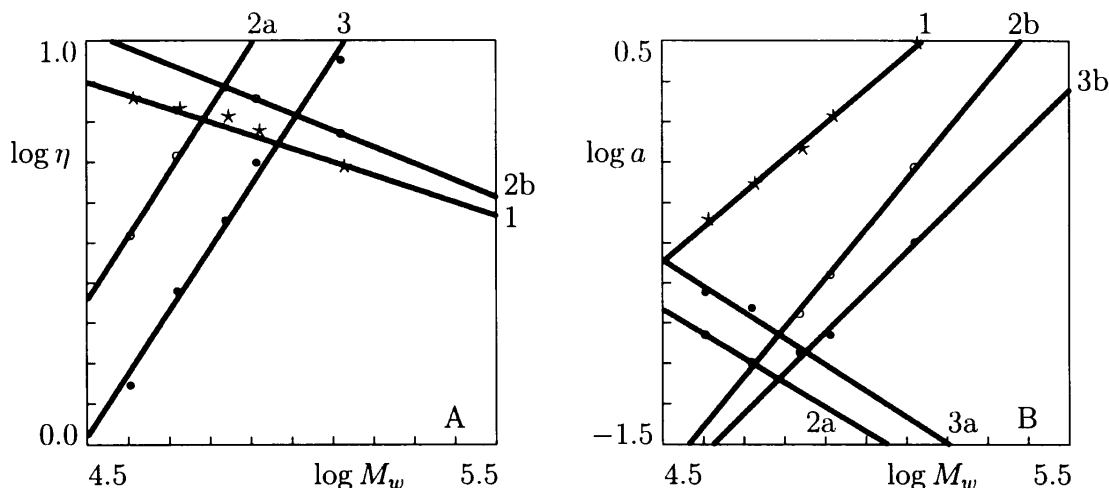
Figure 3: The dimensionless parameters η (A) and a (B) versus molecular weight M_w g/mol for ethylene-octene copolymer CGCT87 at $T = 0$ (stars), $T = 25$ (unfilled circles) and $T = 40$ °C (filled circles). Symbols: treatment of observations (26). Solid lines: approximation of the experimental data by the functions $\log \eta = \eta_0 + \eta_1 \log M_w$ and $\log a = a_0 + a_1 \log M_w$. A: Curve 1: $\eta_0 = 2.38$, $\eta_1 = -0.33$; curve 2a: $\eta_0 = -6.77$, $\eta_1 = 1.58$; curve 2b: $\eta_0 = 2.87$, $\eta_1 = -0.41$; curve 3: $\eta_0 = -6.99$, $\eta_1 = 1.56$. B: Curve 1: $a_0 = -8.27$, $a_1 = 1.71$; curve 2a: $a_0 = 4.61$, $a_1 = -1.21$; curve 2b: $a_0 = -12.67$, $a_1 = 2.45$; curve 3a: $a_0 = 5.26$, $a_1 = -1.30$; curve 3b: $a_0 = -10.78$, $a_1 = 2.01$

is found by the least-squares technique. Results of numerical simulation are depicted in Fig. 1. To calculate Σ, we determine the parameter $\gamma = \tilde{e}_{max}/(1 - \tilde{n}_{max})$, where $\tilde{e}_{max}$ and $\tilde{n}_{max}$ coincide with $\tilde{e}$ and $\tilde{n}$ at the breakage point ($\epsilon = \epsilon_{max}$) found by integration of Eqs. (14) to (16) at $\vartheta = 0$ (maximal strain is reached for chains directed along the elongation axis). Multiplying E by γ and using Eq. (14), we find the quantity $E\gamma = \frac{1}{2}\rho\mu\Xi\Delta$. Bearing in mind that $\Xi = M_e^{-1}$ and utilizing Eq. (1), we obtain $\Sigma = 2E\gamma/\rho$. The quantities E, Σ, η and a are plotted in Figs. 2 and 3 as functions of molecular weight M_w.

Discussion and conclusions

A model has been derived for the isothermal stress-strain response and fracture of elastomers. Adjustable parameters in the constitutive equations are found by matching observations for ethylene-octene copolymer. The essential advantage of our model compared to the slip-link theory (29) and its modifications (30) is that it contains fewer experimental constants and ensures fair agreement between experimental data and results of numerical simulation up to the rupture point (Fig. 1), whereas the conventional approach fails to correctly describe observations at $\epsilon \geq 6$ [Fig. 13 in Ref. (29)]. It is demonstrated that

1. Young's modulus E increases with molecular weight (which is associated with the growth in the number of entanglements) and decreases with temperature (which confirms the applicability of the concept of rigid-rod networks, because conventional theories of rubber elasticity imply an increase in elastic moduli with temperature),

2. the critical strength per bond decreases with temperature [in agreement with conventional observations (6,25)] and increases with molecular weight,

3. the rate of transformation from the flexed to extended conformations of bonds, a, decreases with temperature (a decrease in the rigidity per bond, μ, results in a decrease in its mechanical energy with temperature and makes the *trans-cis*

transition energetically unfavorable) and grows with molecular weight (except for polymers with low molecular weight),

4. the parameter η decreases with molecular weight at low temperature, $T = 0$, and increases at high temperature, $T = 40$ °C, which may be explained by the fact that at low temperatures neighboring chains prevent unrolling of individual macromolecules, while at high temperatures the effect of environment weakens.

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