Long-Time Relaxation of Polymer Networks

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ABSTRACT: A naive single-chain approximation of the topological constraint release of polymer network strands over the whole time region is discussed. In the long-time limit, the net relaxation of the whole network is predicted to follow the empirical Thirion–Chasset relation. A linear cross-link dependence of the characteristic relaxation time has been found. Further, some common features to random hopping models in disordered materials could be examined.

Introduction

Elastomers undergo long-time relaxation processes in stress relaxation and creep experiments.[1–4] Molecular interpretations of the long-time relaxation process are based on controversial assumptions and have been given in the following contexts:

(i) Relaxation of dangling ends:[5–7] In this analysis, each dangling chain is confined by other chains in a virtual tube from which it is able to escape by a diffusion of its free end along the chain contour. Curro et al. assumed a reptation mechanism to describe the diffusional behavior of the free ends,[5,6] while Gaylord et al. preferred a continuous-time random walk model.[7] The different models differ in their prediction of the cross-link density dependence of the power law exponent.

(ii) Slow-moving network modes that may have longer relaxation times than those attributable to dangling ends:[8] These conclusions were drawn by Neuburger and Eichinger from computer simulations of the relaxation time spectra of end-linked random networks. The slow modes are caused by small entropic force constants of the Rouse-like equations of motion of the network. The simulation results indicate that such small force constants seem to be frequent in networks with a great amount of defects (e.g., dangling ends).

(iii) Rouse dynamics of moderately cross-linked network chains which obey an exponential length distribution:[9] The model assumes the separation of time scales between chain motion and the motion of cross-linking points. A broad distribution of time scales of the individual network strands produces nonexponential decay laws even when the single processes are governed by a simple exponential behavior. A stretched exponential law is derived, with an exponent of 1/3.

(iv) Topological constraint release effects of network strands:[10–12] The model rests on the picture that each coil within the network contains many other coils. The overall affine elastic behavior of the network is the result of a cooperative unfolding process in which the deformation of any individual network chain could be smaller than the deformation behavior of the corresponding phantom model.[13]

The constraint release of network strands was originally introduced to allow a description of the strong swelling dependence of the constraint contribution to the elastic free energy of polymer networks.[10] Later, this mechanism was applied to the explanation of the long-time behavior of creep experiments.[11,12]

The evolution of the retardation spectrum and tensile compliance of different types of networks and with increasing cross-linking density has been investigated in ref 12. In all cases, the following behavior has been observed:

(i) With increasing density of network chains, ν, the form of a short-time spectrum maximum and its relative distance to the glass transition time position do not change.

(ii) The form and the time position of the slow relaxation process depends strongly on ν according to $\log \tau_c = -\alpha \log \nu$. Here, τ_c denotes the retardation time at which the spectrum maximum occurs. The value of α depends on the polymer type of which the network is built.

These experimental evidences led to the very crude picture that, after a distortion of the sample, a cooperative relaxation in the rearrangement of the cross-link positions takes place. As elementary steps, we assume that the averaged wobble motion of fluctuating junctions leads to the rearrangement process and, as a result, the end-to-end vector of network strands rotates about its mean position. This process leads to a decrease of the deformation dependence of the topological constraints. In the configurational tubelike approach, the basic mechanism is mainly a weakening of the deformation dependence of the tube diameter.[10] This deformation dependence has been found as follows: $d_\mu = d_0\alpha_\mu^{1/2}$, where d_0 denotes the undeformed tube radius and d_μ ($\mu = x, y, z$) denotes its deformed dimension.[10,23,24] The microscopic network chain deformation $\alpha_\mu = \lambda_\mu^{\beta_e}$ connects the macroscopic deformation of the sample, λ_μ, with the equilibrium constraint release parameter β_e ($0 \leq \beta_e \leq 1$). It characterizes the final (equilibrium) state of the relaxed microscopic network chain deformation. The value of β_e depends on the amount of solvent, sol fraction, network defects, and cross-link density.[12] The time dependence of the release parameter, $\beta(t)$ (with $\beta(t \simeq \tau(N)) \simeq \beta_e$), has been found to be the source of the time dependence of the tube dimension and, at least, the constraint contribution to the modulus. The time $\tau(N)$ is the characteristic time of the constraint release process of a single network chain with N segments. Although we have no microscopic theory of the relaxation of obstacle-enclosing but ramified cyclic network meshes,[14] we assume the knot arrangement process to be a quasi-free diffusion of branched f-star molecules over a distance d_0. Here, d_0 is the mean lateral dimension of the configurational tube, and f denotes the functionality.[10] In this sense, the following characteristic time of the constraint release process of a single network

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chain with N segments has been proposed:[11,12]

$$\tau(N) = \tau_0(N/N_e)^{\alpha} \exp(kN/N_e) \tag{1}$$

In eq 1 we have used the exponential law for the characteristic relaxation time of a melt of branched f-star molecules.[14] We have modified the preexponential factor by introducing a fit parameter α to express the higher cooperativity of networks.

N_e is the number of segments between two successive entanglement points, and α and k ($\simeq 1$) are material constants. Different values of α (3–12) are found for different elastomers if experimental creep data are discussed within our model.[12,13] The time τ_0 corresponds to the characteristic time of the fast relaxation process which is independent of the cross-link density.[12]

Equation 1 needs a somewhat more detailed justification. In the case of branched molecules, the reptation mode is strongly hindered by branching. Several proposed theoretical treatments essentially rely upon the same physical idea: To renew its configuration, an arm must retract completely inside its tube, and the rate of such events is given by the Boltzmann weight of such a retracted configuration.[25–27] This leads to the characteristic reptation time $\tau_{\mathrm{rep}} \sim A(N) \exp(k'N/N_e)$. The prefactor is not known precisely but is not essential in the melt case. We assume that the preexponential factor becomes essential in the case of weakly cross-linked networks and expresses the more strongly hindering of the network chain with largely fluctuating but fixed ends. The fit parameter α expresses the higher cooperativity of networks and depends on the functionality and the polymer type.

The purpose of our paper is threefold. First, we give a crude explanation of the empirical power law relaxation of the mechanical stress and derive it in the long-time limit on the basis of eq 1. Second, we explain the power law dependence of the characteristic slow relaxation time on cross-link density. Further, we show, however, some similarities to models of anomalous relaxation processes in random media with energetic disorder.

Theory

In the case of a stress relaxation experiment, the relative change of the shear modulus becomes

$$\Delta(t) \equiv \frac{G(t) - G_e}{G_e} = \phi(t) \tag{2}$$

where G_e is the equilibrium modulus and $\phi(t)$ is the overall relaxation function. The analogous expression for the creep compliance, $J(t)$, reads in the long-time limit as follows:

$$J(t) = G_e^{-1}\phi(t)^{-1} \tag{2a}$$

We assume that a single relaxation process of a network mesh—according to the proposed constraint release mechanism—is given by

$$\varphi_N(t) = \varphi_0 \exp(-t/\tau(N)) \tag{3}$$

Then the average relaxation $\phi(t)$ is

$$\phi(t) = \int_0^{\infty} \mathrm{d}N\, \varphi_N(t) w(N) \tag{4}$$

The probability that a network chain of a randomly cross-linked network has N segments is described by the Poisson-like distribution

$$w(N) = \bar{N}^{-1} e^{-N/\bar{N}} \tag{5}$$

This distribution function has now been found in numerical simulations of Duering and Kremer in randomly cross-linked systems.[15] Here, $\bar{N} \sim \nu^{-1}$ is the mean segment number of network strands and ν denotes the cross-linking density. The distribution of N leads to many different time scales which produce the net effect on the relaxation behavior: Complex systems containing many different time scales appear to relax slower than exponentially when perturbed.[16]

Inserting eqs 1, 3, and 5 into eq 4 leads to the expression

$$\phi(t) = \phi_0 n_e \int_0^{\infty} \mathrm{d}x \exp(-(t/\tau_0)x^{-\alpha}e^{-x} - n_e x) \tag{6}$$

$$n_e \equiv N_e/\bar{N}, \qquad x \equiv N/N_e$$

The N dependence of φ_N on the right-hand side of eq 6 is mainly attributed to the exponential term of $\tau(N)$. Therefore, we may replace $x^{-\alpha}$ by its mean value $\bar{x}^{-\alpha} = (\bar{N}/N_e)^{-\alpha} = n_e^{\alpha}$. We then obtain

$$\phi = \phi_0 n_e (t/\tau_0)^{-n_e} (n_e^{\alpha})^{-n_e} \Gamma(n_e,(t/\tau_0)n_e^{\alpha}) \tag{7}$$

with $\Gamma(x,y)$ being the incomplete gamma function. We will compare the exact expression eq 6 with the approximate solution eq 7 later in the discussion.

Mathematically, eq 7 is equal to the average correlation function of an anomalous relaxation process in random media with energetic disorder, if the distribution of the energy levels is assumed to be Poisson-like.[17] In the hopping models in random media with energetic disorder the quantity N plays the role of the height E of an energy barrier and N_e corresponds to the temperature $k_B T$.

In the long-time limit eq 7 yields the power law relaxation

$$\phi(t) \simeq \phi_0 (t/\tau_c)^{-n_e} \tag{8}$$

with the characteristic relaxation time

$$\tau_c = (\tau_0/n_e^{\alpha}) = \tau_0(\bar{N}^{\alpha}/N_e^{\alpha}) \sim \nu^{-\alpha} \tag{9}$$

Discussion

(a) Equation 8 has the same form as the empirical Thirion–Chasset relation.[1] The exponent $n_e = N_e/\bar{N}$ can be expressed by the mean lateral dimension of the confining configurational tubes, d_0, as follows:[10]

$$n_e = \frac{d_0^2}{l^2\bar{N}} = \frac{K^2(n_s l^3)^{-1} M_s}{\rho} \tag{10}$$

Here, n_s is the number density of the segments, l is the statistical segment length, and M_s is its molecular mass. The quantity ρ denotes the polymer density and ν the cross-link density (in 10^{-4} mol cm^{-3}). In the case of natural rubber we find with $K = 5.8$[10,18] the relation $n_e \simeq 0.12\nu$, which is in reasonable agreement with available experimental data (ref 5, Figure 2). Equation 9 reflects the dependence of the time position of the investigated slow relaxation process on cross-link density.[3,12]

(b) The average relaxation time of our model reads

$$\langle \tau(N) \rangle = \int_0^{\infty} w(N)\tau(N)\, \mathrm{d}N \tag{11}$$

and gives with eq 1

$$\langle \tau(N) \rangle \simeq \tau_0 n_e \alpha! (n_e - 1)^{-(\alpha+1)} \tag{12}$$

This relaxation time is termed the average "escape time" in the corresponding random hopping model.[17] In this latter case the motion of a particle is frozen, hence $\langle \tau \rangle$ diverges, if the temperature is below a transition temperature, $k_B T^* = E$. The average relaxation time $\langle \tau(N) \rangle$ diverges at $n_e = \nu/\nu_{\mathrm{crit}} = 1$. It is physically clear that $\langle \tau$-

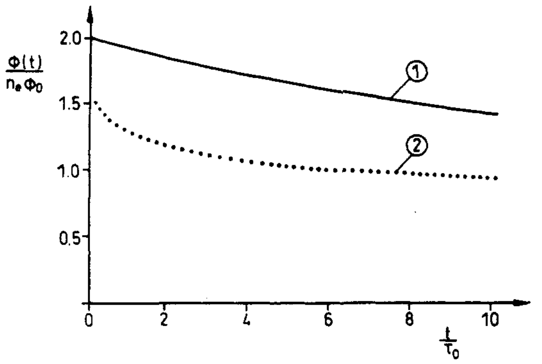

Figure 1. Comparison of the numerical evaluation of eq 6 with the approximation eq 7 in the short-time limit. The dotted line is the exact numerical result (curve 2). Curve 1 is the approximation. The curves are nearly parallel in this time domain.

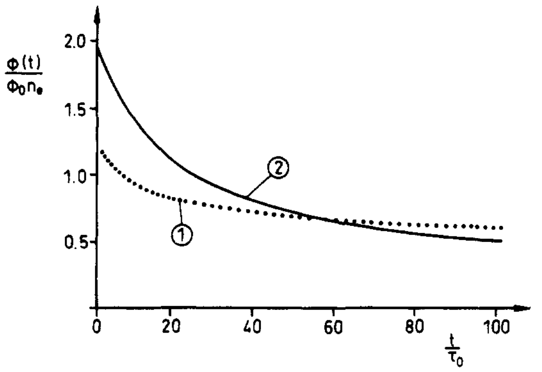

Figure 2. Same as Figure 1 in the long-time limit $0 < t/\tau_0 < 100$. Exact enumeration 1 and approximation 2 agree well for large times. In both figures $n_e = 0.5$ is chosen.

$\langle N \rangle$) is always infinite in our model because it assumes a strongly entangled network with $n_e < 1$. A dynamical phase change is predicted for $n_e > 1$ ($\bar{N} < N_e$) where Rouse-like dynamics has to be assumed.[19] Our model is not valid in this case.

(c) We report on the approximation which led to the Thirion–Chasset law. We obtain eq 7 by replacing $x^{-\alpha}$ by its average value n_e^{α}. In Figure 1 we compare the exact relaxation function eq 6 with the Thirion–Chasset law for short tims $0 < (t/\tau) < 10$. We see that the curves are almost parallel in that time domain. This shows that the Thirion–Chasset exponent is predicted well but not the prefactor. For larger times $0 < (t/\tau) < 100$ the curves become close to each other (see Figure 2) and the approximation works quite well. For very large times $t/\tau_0 > 100$ the curves begin again to differ slightly.

In the following, we compare our theoretical results with the experimental findings. Thereby we will find that the physics of long-time processes in networks will still remain under controversial discussion.

(d) In ref 11 the relaxation function has been assumed to be a fractional-exponential law (KWW function). Gaylord et al. have shown that the fits of power law relaxation and KWW relaxation of stress relaxation data are practically indistinguishable.[7] Both types of decays are typical for a broad variety of disordered materials displaying relaxations which cannot be expressed in terms of a single decay rate. Such decay patterns may arise from quite different microscopic dynamics.[16]

The connection between power law relaxation and fractional-exponential relaxation becomes more transparent remembering that, from a phenomenological point of view, both decay patterns have a common origin. They are limiting cases of a more general hyperlogistic model which is of relevance for aggregated growth or extinction processes in complex systems.[20]

(e) Thirion and Chasset already noted that deviations from the power law behavior are often observed at long times $t \gtrsim 10^3$ s. These deviations are more pronounced for the more highly cross-linked networks (i.e., the natural rubber samples I and J with cross-link densities $\nu = 1.2 \times 10^{-4}$ and 1.69×10^{-4} mol·cm^{-3}, respectively). These observations were confirmed by McKenna and Gaylord, who reexamined the experimental data of Thirion and Chasset in a recent publication.[21,28]

We believe that, besides the predicted differences between exact and approximated calculations in our model, a totally different mechanism seems to be important to explore the deviations: Figure 3 in ref 21 shows the double-logarithmic representation of the first-derivative approximation to the relaxation spectrum versus time for different samples. Deviations from linearity are more pronounced for the natural rubber, but less for the styrene–butadiene rubber (SBR). The differences between these two kinds of rubber are quite apparent. It is known that natural rubber undergoes a strain-induced crystallization under load. This effect leads to additional elastically effective (physical) cross-linking points within the sample. This type of junction may partially vanish during the relaxation experiment at longer times. Then a faster drop of the mechanical stress would be observed compared with the Thirion–Chasset law.

We further note that the highly cross-linked NR samples (I and J in Figure 3 and the long-time end of the master curve in Figure 5)[21] have values ν of the order of the critical density $\nu_{\text{crit}} \simeq 2 \times 10^{-4}$ mol·cm^{-3} (Figure 21a in ref 12) where short-time and long-time relaxation processes begin to overlap. The source of the short-time relaxation is a totally different mechanism (Rouse-like dynamics of strands between entanglements) that does not follow anomalous relaxation behavior. Therefore, the relaxation data of highly cross-linked samples cannot predict the Thirion–Chasset law.

(f) McKenna and Gaylord confirmed a time–cross-link density superposition for networks and concluded that any power law representation of the relaxation behavior must have an exponent that is independent of cross-link density in order to be compatible with the time–cross-link density correspondence.[21] This is in contrast to the paper of Curro and Pincus, who found a linear dependence of n_e on ν.

We predict a linear relation $n_e \sim \nu$ which is compatible with the time–cross-link density superposition behavior according to eq 9. This is a main result of the presented model. Equation 9 corresponds to the suggestion of Plazek that τ_c can be written as $\tau_c(T,\nu) = \tau_c(T,\nu_0)a_\nu$.[22] Here, ν_0 refers to the reference cross-link density and a_ν represents the shift factor. Plazek observed $a_\nu = (\nu/\nu_0)^{-\alpha}$, i.e., a power law in accordance with the experimental findings in refs 3 and 12 and in accordance with the theoretical prediction eq 9.

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