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Relaxation Processes in the Transition Zone

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Relaxation processes in the transition zone are reviewed and analyzed in terms entropic and energetic components of modulus and stress. Limitations of Rouse Theory and time temperature superposition are discussed.

KEY WORDS Relaxation process, transition, time-temperature superposition.

INTRODUCTION

It is possible to determine three general regions in the viscoelastic behavior of elastomers: a transition zone from glass-like to rubber-like state, a plateau and terminal zone. Each region has a characteristic segment of the relaxation spectrum. This correspondence is illustrated in Figure 1, which shows the relaxation spectrum of natural rubber over a wide time interval.

The first significant success in the understanding of relaxation processes in the transition zone was achieved by Rouse¹ and subsequent investigators^{2,3} on the basis of the model of submolecules. This theory, resulting from the concepts of the purely entropic nature of elasticity, correctly describes the shape of the relaxation spectrum in the long-time part of the transition zone and provides a theoretical foundation for the principle of the temperature-time reduction.⁴ Its main limitation arises from the supposition that equilibrium inside the submolecules has already been reached by the moment of observation. This excludes from consideration the short relaxation times that represent a significant portion of the relaxation spectrum. The theory thus has limited applicability in the range of short times, and according to Williams,⁵ the theory can only claim to describe a small part of the transition zone when the unequilibrium modulus is below 1 MPa.

Nevertheless the experimental data are usually compared with the theory of submolecules over the entire transition zone⁴ which follows from the broad-based assumption about the purely entropic nature of elasticity. This supposition underlies the principle of temperature-time reduction when the reduced stress, $\sigma(t/a_T, T_0)$, is determined by the formula

$$\sigma \left(\frac{t}{a_T}, T_0 \right) = \frac{\sigma(t, T) T_0 \rho_0}{T \rho} \quad (1)$$

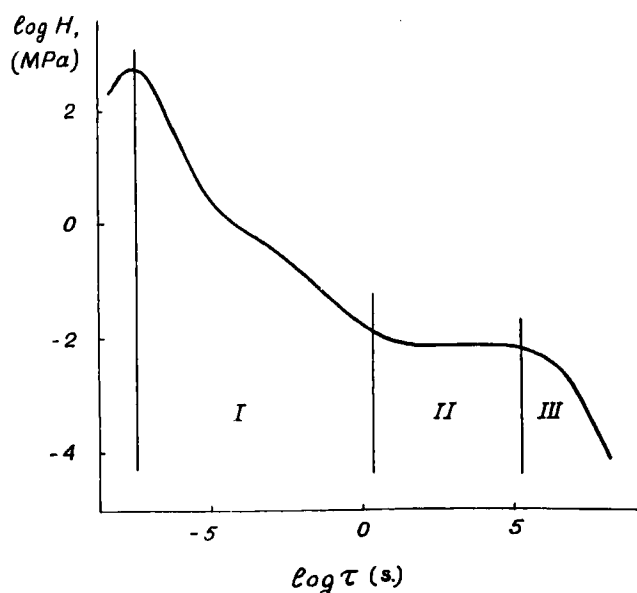


FIGURE 1 The relaxation spectrum of natural rubber reduced to 25°C. I = transition zone, II = plateau zone and III = terminal zone.

Here, $\sigma(t, T)$ is the measured stress, a_T is the constant of the reduction, T_0 and ρ_0 are the temperature of the reduction and the density of the polymer at this temperature; T and ρ are the temperature at which the measurements were taken and the density corresponding to it.

However, in the transition zone, where the modulus varies by 1000 times and more, there is a change of the elastic nature from a purely energetic one, corresponding to a glass-like state, to a completely entropic one in the rubber-like state. These statements of a purely qualitative character were made some time ago,⁶ but as yet no attempt has been made to experimentally divide the stress into an energetic component, $\sigma_e(t)$, and an entropic one, $\sigma_s(t)$, and to evaluate the maximum value of $\sigma_s(t)$.

The first step in this direction was calculation of the relaxation spectrum in the transition zone on the basis of the so-called discrete or lattice models.⁷⁻¹⁰ This theory also considers only the entropic mechanism of elasticity, but it does take into account all the relaxation times connected with conformation rearrangements in the polymer chains. The theory predicts the same form of the relaxation spectrum as the Rouse theory, but is applicable over a time interval half again to twice as long. According to this theory the maximum value of the unequilibrium modulus can be considered to be the maximum value of the entropic component in the transition zone. From this the formula becomes

$$E_{s,\max} = 3 \frac{RT\rho}{M_0} \quad (2)$$

where R is the universal gas constant, and M_0 is the molecular mass of the smallest

chain section taking part in the elementary act of the conformation rearrangement. In the case of polyethylene, using the molecular mass of the CH_2 group, we obtain $E_{s,\text{max}} = 480$ MPa, which is substantially lower than the maximum value of the unequilibrium modulus in the transition zone. For other polymers this value will be lower still due to greater values of M_0 . It should also be noted that this is an upper bound estimation of $E_{s,\text{max}}$. The actual values of $E_{s,\text{max}}$, as will be discussed further on, are substantially lower.

The first attempt at the experimental division of the stress in the transition zone into energetic and entropic components was made¹¹ by comparing the data on the stress and birefringence relaxation in butadiene-acrylonitrile rubber.

THEORY

The Bruster law is known to be valid for polymers in both the rubber-like state and the glass-like one. There is thus proportionality between the value of birefringence, Δn , and stress, σ :

$$\Delta n = c\sigma \quad (3)$$

In addition, Bruster's constant, c_e , for the glass-like state is lower by a factor of 10^2 than that for the rubber-like state, c_∞ . It thus follows that the birefringence in

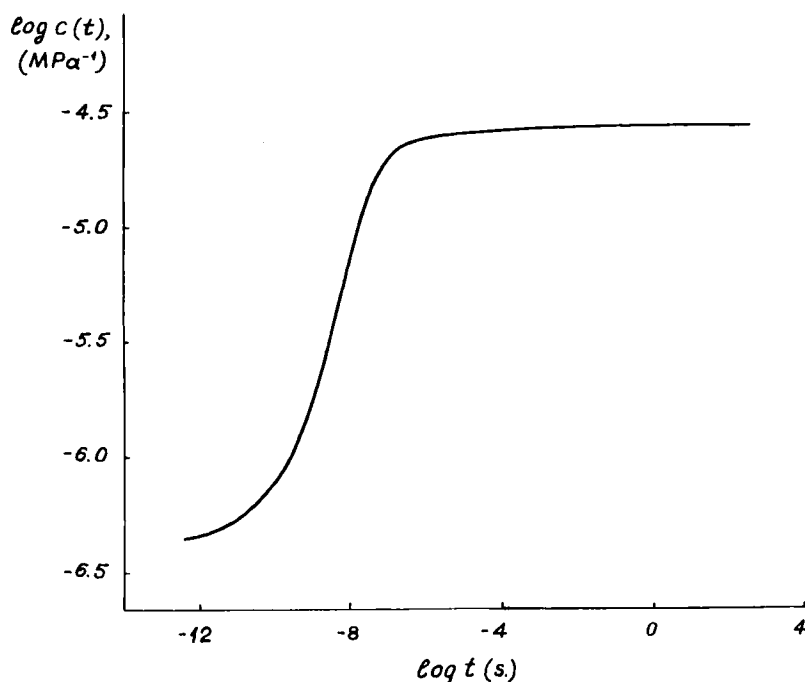


FIGURE 2 Reduced master curve of non-equilibrium stress-optical coefficient $c(t, T_0)$ for butadiene-acrylonitrile vulcanizate at $T_0 = 25^\circ\text{C}$.

the glass-like state has distortion nature: it is associated with the change of the interatom distances, while in the rubber-like state it is determined by the orientation of the chain links. In dynamic testing Δn and σ change in phase in both states. While studying the dynamic birefringence Read¹² found that in the transition zone a phase shift occurs between Δn and σ , with Δn taking an intermediate position in phase between σ and strain ϵ . In the transition zone Bruster's constant, calculated from the data on the relaxation of Δn and σ , varies from c_e to c_∞ , as shown in Figure 2, borrowed from previous work.¹¹ The above behavior of Δn can be described proceeding from the assumption that in the transition zone there are simultaneously two mechanisms of elasticity and birefringence and the relation between them changes at various stages. If we furthermore assume the additivity of these mechanisms, then we obtain:

$$\Delta n(t) = \Delta n_e(t) + \Delta n_s(t) \quad (4)$$

where $\Delta n_e(t)$ and $\Delta n_s(t)$ are the distortion and orientation components of the birefringence, respectively.

On the basis of the submolecule theory Read¹³ showed that Bruster's law should also be observed for the non-equilibrium state with the same optical coefficient of stress as for the equilibrium. This allows us to write

$$\Delta n_s(t) = c_s \sigma_s(t) \quad (5)$$

where

$$c_s = c_\infty - c_e = \frac{2\pi}{45kT} \frac{(\bar{n}^2 + 2)^2}{\bar{n}} (\alpha_1 - \alpha_2) \quad (6)$$

is the optical coefficient of stress according to the theory of rubber-like elasticity, \bar{n} is the average value of refractive index, $\alpha_1 - \alpha_2$ is optical anisotropy of a statistical chain segment, and k is Boltzmann's constant.

Unlike the orientation component, the distortion component of the birefringence should be proportional to the total stress:

$$\Delta n_e(t) = c_e \sigma(t) \quad (7)$$

since it causes variation of the interatom distances. That is why a small distortion component should also be present in the rubber-like state, which accounts for the difference between c_s and c_∞ .

Substituting (5) and (7) in (4) we find:

$$\Delta n(t) = c_e \sigma(t) + c_s \sigma_s(t) \quad (8)$$

or

$$c(t) = c_e + c_s \frac{\sigma_s(t)}{\sigma(t)} = c_e + c_s \frac{E_s(t)}{E(t)}, \quad (9)$$

where $E(t)$ is the unequilibrium modulus, and $E_s(t)$ is its entropic component.

The latter relation provides an opportunity to experimentally determinate E_s from measurements of $E(t)$ and $c(t)$ in the transition zone:

$$E_s(t) = \frac{c(t) - c_e}{c_s} E(t) = \frac{c(t) - c_e}{c_x - c_e} E(t) \quad (10)$$

Unfortunately it is impossible to obtain data for $E(t)$ and $c(t)$ in the whole transition zone without the use of the temperature-time reduction. Because of this constraint our derivation needs certain alterations, specifically a correction for the kinetic factor. The modification should not be made to the entire unequilibrium modulus, $E(t)$, as is normally done, but only to its entropic component, $E_s(t)$. Thus instead of (1) we have:

$$\begin{aligned} E\left(\frac{t}{a_T}, T_0\right) &= \frac{\rho_0}{\rho} \left[E(t, T) - E_s(t, T) + \frac{T_0}{T} E_s(t, T) \right] \\ &= \frac{\rho_0}{\rho} \left[E(t, T) + \left(\frac{T_0}{T} - 1\right) E_s(t, T) \right] \end{aligned} \quad (11)$$

A similar situation arises with the temperature-time reduction of $c(t)$. In this case c_e can be considered independent of the temperature, and c_s , according to (6), inversely proportional to the absolute temperature. No correction for density variation should be made in this case, since both Δn and E are proportional to T . Then, according to (9), we have:

$$\begin{aligned} c\left(\frac{t}{a_T}, T_0\right) &= c_e + \frac{T}{T_0} c_s(T) \frac{\frac{T_0}{T} E_s(t, T)}{E(t, T) + \left(\frac{T_0}{T} - 1\right) E_s(t, T)} \\ &= c_e + c_s(T) \frac{E_s(t, T)}{E(t, T) + \left(\frac{T_0}{T} - 1\right) E_s(t, T)} \end{aligned} \quad (12)$$

Equations (11) and (12) were used for plotting the reduced master curves of $E(t)$ and $c(T)$ in the transition zone. These data were then used with Formula (10) to back-calculate the $E_s(t)$ dependence.

EXPERIMENT

Experimental equipment for the measurement of relaxation of $\sigma(t)$ and $\Delta n(t)$ and methods for processing of results are described in detail elsewhere.¹⁴ Later in this work are presented only the final results obtained by I. I. Vishnjakov and I. P. Pavlova. Figure 3 shows the reduced master curves of $E(t)$, $E_s(t)$ and $E_e(t) = E(t) - E_s(t)$ for the SKN-40 vulcanizate. Figures 4–7 show the same plots for the vulcanizates of SKDL, NR, Butyl and SKMS-30 ARK, all with similar results. The entropic component, $E_s(t)$, passes through the maxima. The energetic component, $E_e(t) = E(t) - E_s(t)$, falls abruptly in the short-time part of the transition zone, decays further in the rubber-like state and approaches a very low but finite value in the equilibrium. The maximum values of $E_s(t)$ lie within 15–30 MPa, or a half to full order of the magnitude lower than the values predicted by the theory based on the lattice model. Table I compares experimental and theoretical values of $E_{s,max}$ for a number of polymers along with the M_0 values used to calculate the theoretical values. The $E_{s,max}$ values listed for NR, polyacetaldehyde, and polymethylacrylate were calculated from data published by Read.¹² The agreement of the results for

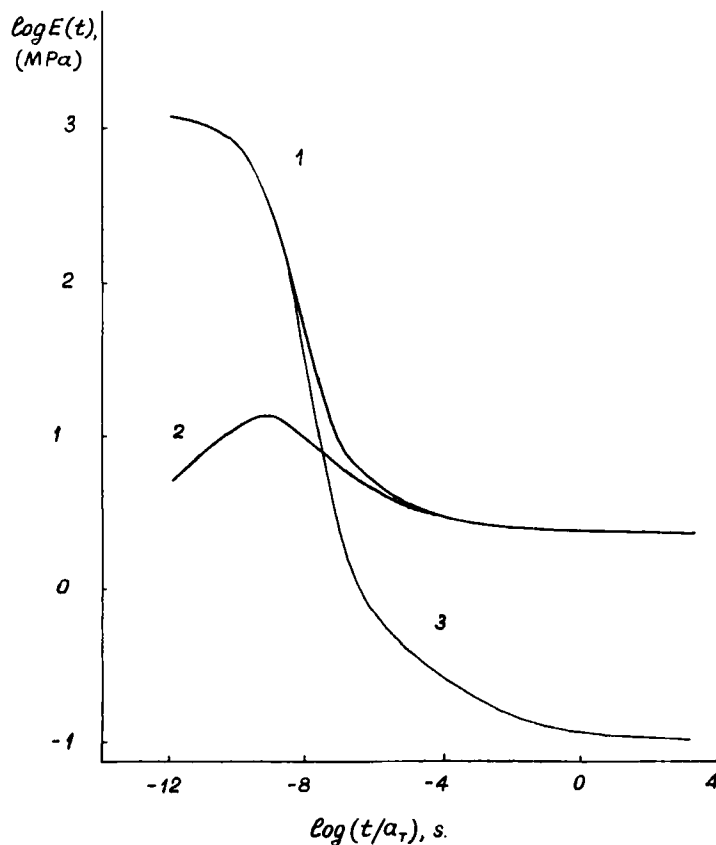


FIGURE 3 Reduced master curves of $E(t, T_0)$, $E_s(t, T_0)$ and $E_e(t, T_0) = E(t, T_0) - E_s(t, T_0)$ for butadiene-acrylonitrile vulcanizate at $T_0 = 25^\circ\text{C}$. 1 = $E(t, T_0)$, 2 = $E_s(t, T_0)$ and 3 = $E_e(t, T_0)$.

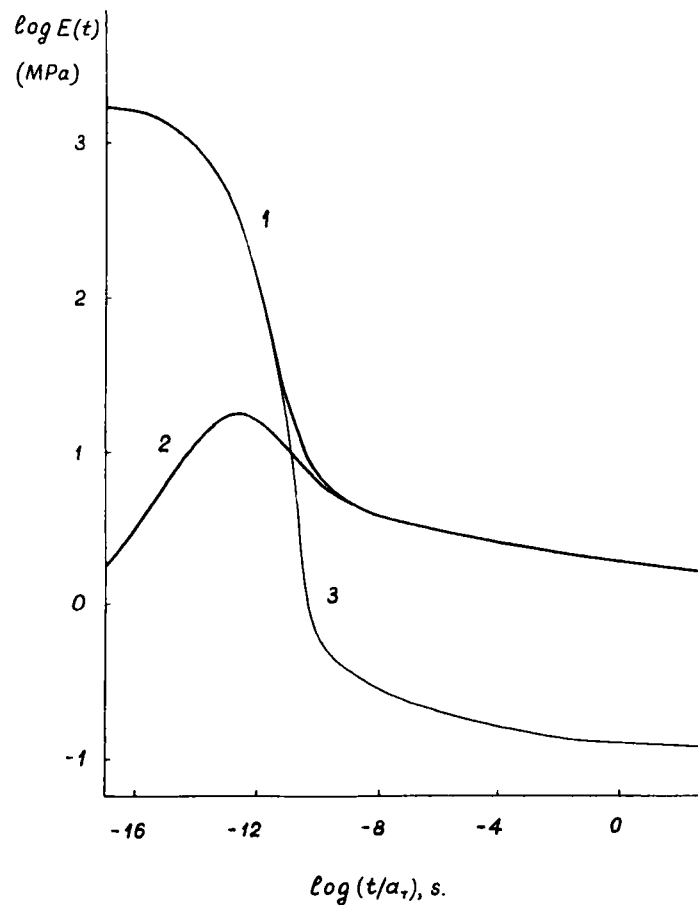


FIGURE 4 Reduced master curves of $E(t, T_0)$, $E_s(t, T_0)$ and $E_r(t, T_0) = E(t, T_0) - E_s(t, T_0)$ for vulcanizate of butadiene rubber of lithium polymerization at $T_0 = 25^\circ\text{C}$. 1 = $E(t, T_0)$, 2 = $E_s(t, T_0)$ and 3 = $E_r(t, T_0)$.

NR indicates that the measurements of the relaxation of Δn and the measurements Δn under dynamic conditions give equivalent information.

DISCUSSION

The differences between the measured and calculated values of $E_{s,\max}$ should not be considered as incompatibility between theory and experiment. Theory only gives the upper bound estimation of $E_{s,\max}$, based on the assumption that the relaxation of E_s has not begun yet. In light of the obtained data, the relaxation processes of real polymers in the transition zone can be considered in the following way. At very short times of observation, when conformation rearrangements in the polymer chains have not occurred yet, the chain conformations characterized by the sequence of rotational isomers remain the same as in the undeformed state, i.e. there is practically no change of entropy under strain. In this case the restoring force has

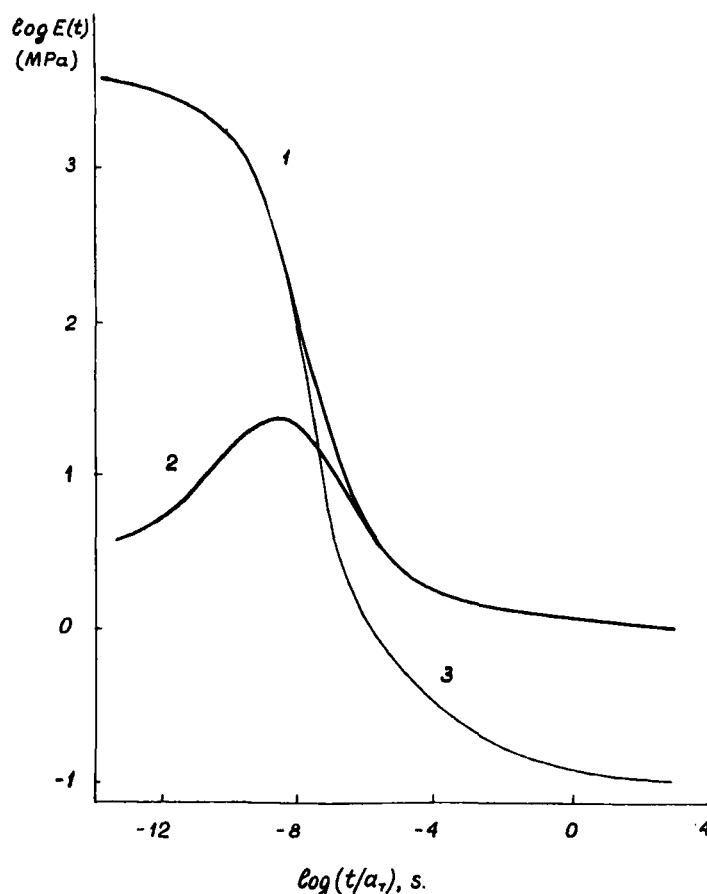


FIGURE 5 Reduced master curves of $E(t, T_0)$, $E_s(t, T_0)$ and $E_e(t, T_0) = E(t, T_0) - E_s(t, T_0)$ for natural rubber vulcanizate at $T_0 = 25^\circ\text{C}$. 1 = $E(t, T_0)$, 2 = $E_s(t, T_0)$ and 3 = $E_e(t, T_0)$.

a purely energetic nature and is associated with the distortion of the valence angles and rotational isomers. Even the first conformation rearrangements reduce the stress in the chains (the distortions of the valence angles and rotational isomers decrease) and the energetic component of the stress decreases. At the same time the chain conformations change and the entropic component of the stresses emerges. The subsequent conformation rearrangements result in further reduction of σ_e and increase of σ_s . But the conformation distribution taking place as a result of the first rearrangements is non-equilibrium, while the subsequent rearrangements move it to equilibrium. Thus, the increase of the number of the conformation rearrangements (increase of the observation time) leads on the one hand to the increase of σ_s due to the deeper conformation changes in the chains, and on the other hand to the decrease of σ_s due to the approach to the chain conformation equilibrium distribution. The competition of these two processes produces the maximum of $E_s(t)$, as shown in Figures 3 to 7. Evidently, with such time variation of σ_s the maximum value of $E_s(t)$ must be substantially lower than the one calculated with the lattice model. The difference between this theoretical calculation and the pro-

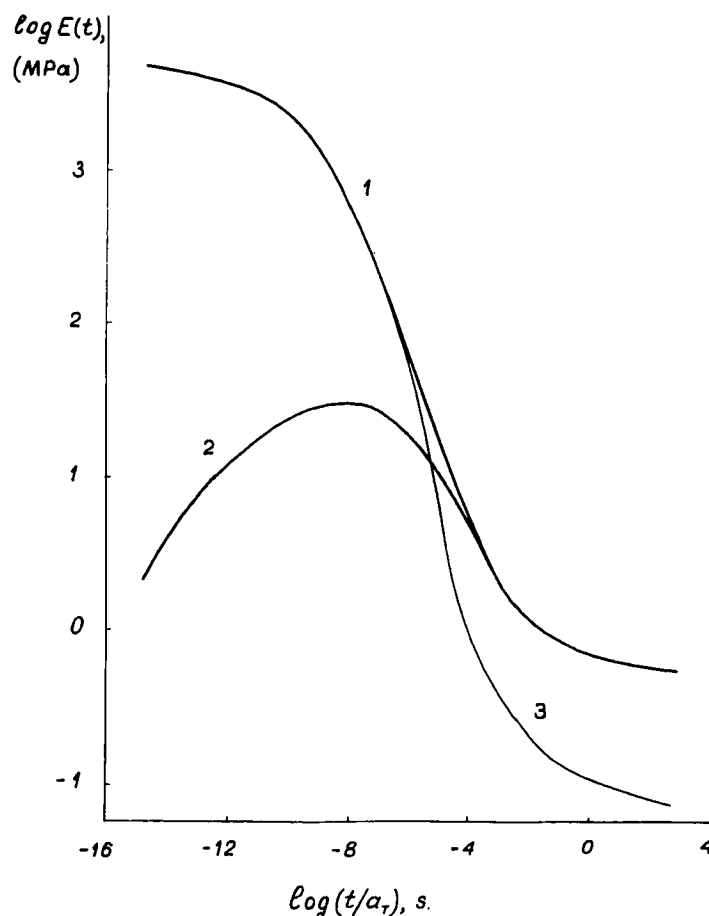


FIGURE 6 Reduced master curves of $E(t, T_0)$, $E_s(t, T_0)$ and $E_e(t, T_0) = E(t, T_0) - E_s(t, T_0)$ for butyl vulcanizate at $T_0 = 25^\circ\text{C}$. 1 = $E(t, T_0)$, 2 = $E_s(t, T_0)$ and 3 = $E_e(t, T_0)$.

cess described above lies in the timing of the chain conformations. The theory assumes that the changes in the chain conformations occur in the course of deformation, that the initial state is far from equilibrium and the nature of elasticity is purely entropic. In the process described above, to the contrary, the chain conformation variation occurs during the stress relaxation in the transition zone. This seems like a more realistic picture.

The process under study can be qualitatively described with the aid of the mechanical model shown in Figure 8. The right-hand part of the model represents non-equilibrium entropic polymer elasticity, $E_s(t)$, as a system of parallel-connected Maxwell elements simulating stress relaxation when the equilibrium conformation distribution sets in. This system is shunted by a viscous element, η , which determines the rate of the rubber-like strain development, i.e. the frequency of the conformation rearrangements. The elastic element, E_e , identified with the equilibrium modulus of elasticity and connected in series, simulates the stretching of the chains due to the distortion of rotational isomers and valence angles.

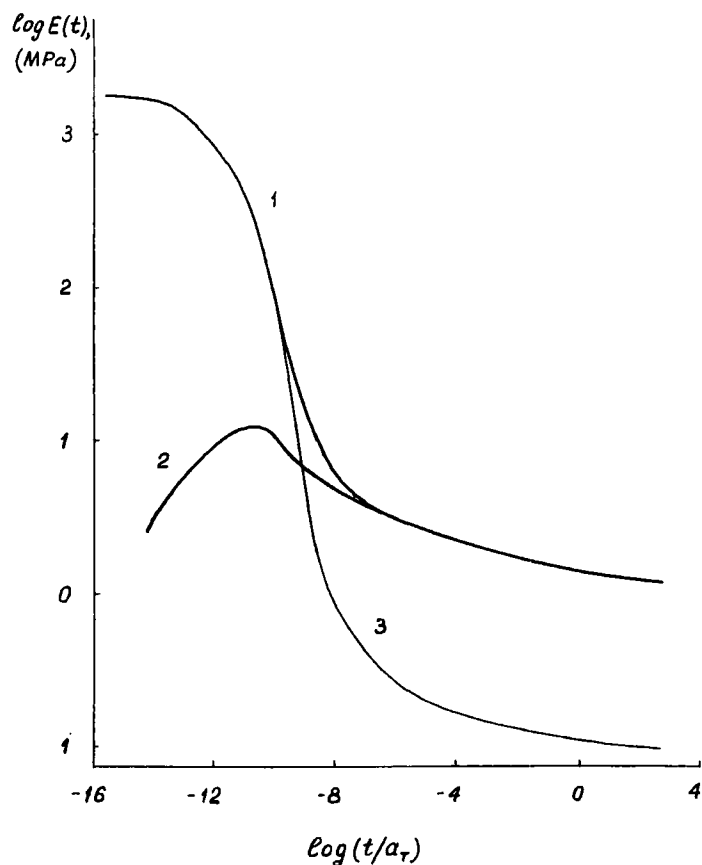


FIGURE 7 Reduced master curves of $E(t, T_0)$, $E_s(t, T_0)$ and $E_e(t, T_0) = E(t, T_0) - E_s(t, T_0)$ for vulcanizate of butadiene-methylstyrene copolymer SKMS-30 ARK at $T_0 = 25^\circ\text{C}$. 1 = $E(t, T_0)$, 2 = $E_s(t, T_0)$ and 3 = $E_e(t, T_0)$.

TABLE I

Experimental and theoretical values of $E_{s,\max}$ for different polymers

Polymer	$\frac{\text{kg}}{\text{m}^3} \times 10^{-9}$	M_0	MPa	
			Theory	Experiment
SKN-40	0.99	21	117	14.1
SKDL	0.91	19	119	18.6
NR	0.93	23	100	23.4
Butyl	0.91	28	80	31.6
SKMS-30 ARK	0.93	44	52	12.6
NR ^a	0.93	23	100	25.0
Polyacetaldehyde ^a	1.20	22	135	24.6
Polymethylacrylate ^a	1.20	43	69	18.0

^aCalculated with the use of the data published by Read.¹²

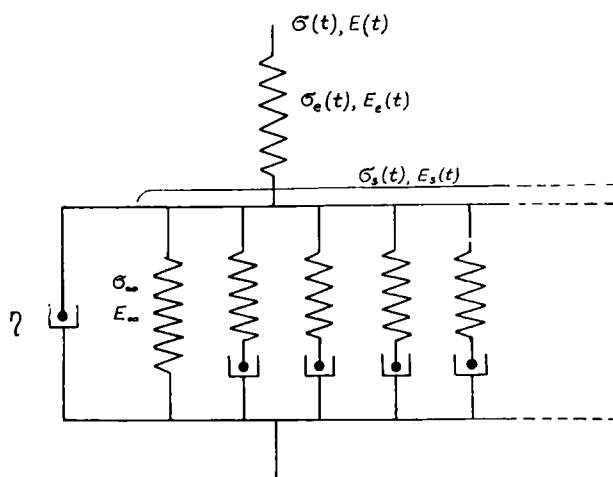


FIGURE 8 Mechanical model for qualitative description of viscoelastic properties of polymer in the transition zone.

Certainly the actual process of stress relaxation in the transition zone is too complicated to be quantitatively described with the aid of such a simple model. It reflects only its own characteristic features and is useful only for qualitative analysis. A quantitative description is possible only on the basis of the molecular theory. As the obtained data show, such a theory should be rebuilt on a fundamentally new basis.

Another important result of this work is indication of the necessity to make corrections in the principle of the temperature-time reduction. Since the entropic component of the stress is only a comparatively small part of the total stress in the transition zone, this correction becomes appreciable. Depending on the ratio of the temperature of reduction to glass-transition temperature, it can result in a decrease of the relaxation spectrum width in the transition zone by 1–2 orders of time (with the corresponding change of its form in the region of short times) compared to the spectrum obtained with the use of the classical principle of the temperature-time reduction.

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