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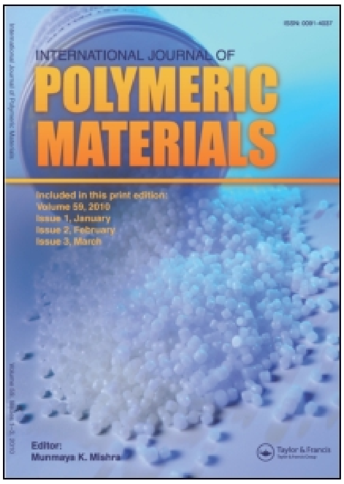

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Polymer Elasticity Nature in the Transition Zone†

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In the zone of transition from the glass-like to rubber-like state the change of polymer elasticity mechanism takes place from entropy to energy nature. On the basis of phenomenological photoelasticity theory in non-equilibrium state the separation method for the energy and entropy components of stress is suggested. It is pointed out that the correction for kinetic factor T/T_0 (T and T_0 are experimental and reduction temperatures, correspondingly) has to be introduced not for the entire stress but for its entropy component only while using the time-temperature reduction principle. The results of combined measurements on stress and birefringence relaxation in butadiene-acrylonitrile vulcanizate are presented within the temperature limits from -26.4 to 25°C and time limits from 0.4 to 1000 sec. From the data obtained the reduced master curves of entropy modulus component and entropy relaxation spectrum have been calculated. The latter has the form in accordance with the predictions of the molecular theory of polymer viscoelasticity.

INTRODUCTION

In the zone of transition from the glass-like to rubber-like state the non-equilibrium (or relaxation) modulus elasticity of polymers, $E(t)$, changes by more than 1000 times. Glass polymer elasticity is of energy nature, i.e. it is connected both with the strain of valent bonds and angles and with a distortion of rotational isomers. Elasticity in rubber-like state is basically of entropy nature and is caused by changes in the conformational set of chains. In the transition zone, therefore, one elasticity mechanism must be replaced by another.

Many years ago[1] these ideas already made it possible to state that pure elastic deformation (caused by the changes in the particle-to-particle distances)

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precedes the rubber-like one. Later Stein[2] in discussing the data on the birefringence in polymers pointed out that the change of Bruster's coefficient in the transition zone is connected with the change of the elasticity mechanism. Summarizing the results of works on dynamical birefringence in the polymers of different chemical structure, Read[3] indicates that these data may serve as a basis for the separation of non-equilibrium stress $\sigma(t)$ into energy $\sigma_e(t)$ and entropy $\sigma_s(t)$ components. Such a separation, however, was not accomplished quantitatively in Read's works, nor in those of other authors. That's why it is impossible to say now what is the ratio between these components at different stages of the equilibrium setting, or give the maximum value of the entropy component, $E_s(t)$, of the non-equilibrium modulus. The paper attempts to answer these questions. But before discussing the possibility of quantitative $\sigma_e(t)$ and $\sigma_s(t)$ separation it is useful to refer to the modern theoretical concepts of the relaxation processes mechanism in polymers.

The first substantial success in describing regularities of relaxation processes in the transition zone was obtained by Rouse[4] and other authors[5,6] on the basis of a submolecule model. This theory proceeding from the ideas about the purely entropy nature of elasticity correctly describes the shape of the relaxation spectrum in the transition zone and theoretically substantiates the principle of time-temperature reduction.[7] Its weak point is the assumption that submolecules are in their equilibrium state during the entire relaxation process. This assumption excludes short relaxation times from the consideration and, as a result, according to an estimation by Williams, submolecule theory application[8] is limited to the range of observation times when a non-equilibrium modulus value doesn't exceed 1.0 Mn/m^2, i.e. only to a small part of the transition zone.

In attempts to overcome this difficulty, Tobolsky and Aklonis[9] postulated that the relaxation spectrum of Rouse type has also to occur in the range of short times, but in this case chain fragment elasticity will not be an entropy one, but will rather be connected with rotations around the single bonds and valent angle distortions. Although this assumption is essentially beyond doubt the theory cannot predict $\sigma_e(t)/\sigma_s(t)$ ratio, or maximum value of $E_s(t)$ due to its phenomenological nature.

The further progress in the theory of the viscoelastic properties of polymers was reached on the basis of so-called discrete or lattice models.[10,11] In this theory as well only entropy mechanism of elasticity is considered, but all the relaxation times which are connected with the conformational rearrangements in the chains are taken into account. According to the theory of discrete chains the maximum value of the non-equilibrium modulus is 100 Mn/m^2.[12]

This value should be considered as an upper estimate of the maximum magnitude of $E_s(t)$ in polymers. As it will be shown below entropy component can never reach this value.

METHOD FOR SEPARATION BETWEEN ENERGY AND ENTROPY COMPONENTS OF STRESS

Let us consider the case of an instantaneous rubber-like polymer stretching followed by stress relaxation in it, taking into account the fact that polymer strain is determined by the sum of the resilient and high-elastic components. Then in accordance with the recent notions concerning the molecular motion in polymers,[13] if an observation time is very short, conformational rearrangements have no time to occur and polymer strain is caused mainly by the distortion of rotational isomers, i.e. by displacement of the angles of rotation around the single bonds of the backbone from the positions corresponding to the minimal potential energy. In this case entropy changes are small, because macromolecule conformations described as a sequence of rotational isomers remains unchanged, and the recovering force is of purely energy nature. The first intramolecular rearrangements lead to the decrease of the potential energy of the system, i.e. to the decrease of the distortion of rotational isomers, but it is followed by a change in the chain conformations. Thus, the energy component of the recovering force decreases (that is the origin of stress relaxation in this range of times), but the entropy component increases. If the process of conformational rearrangements has been profound enough, the energy component becomes infinitesimal, and the relaxation processes in polymer are connected only with the setting of the equilibrium distribution of the chain conformations.

This consideration doesn't contradict the temperature-time reduction principle, since the relaxation of the entropy and energy stress components is caused by the same conformational rearrangements. At the same time it follows that the kinetic factor must be taken into account at time-temperature reduction only for the entropy stress component.

The stress relaxation process in the transition zone is convenient to consider using the model for separation of $E(t)$ into entropy, $E_s(t)$, and energy, $E_e(t)$, components (Figure 1).

The right hand part of the model represents non-equilibrium entropy elasticity of polymer $E_s(t)$, as a system of parallel-connected Maxwell elements, simulating chain stretching at the expense of the conformational rearrangements, and elastic element, E_∞, identified with the equilibrium modulus of elasticity.

This system is shunted by viscous element, η, which determines the velocity of rubber-like strain development. An elastic element $E_e(t)$ simulating stretching of the chains at the expense of the rotational isomer distortions is joined in series to take into account the energy elasticity of polymer.

Let us use this model to describe the non-equilibrium photoelasticity of polymers. The non-equilibrium birefringence $\Delta n(t)$ may be represented as a

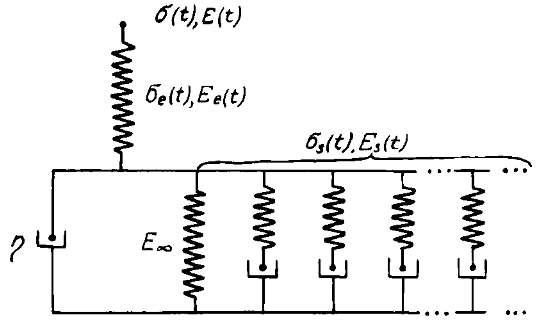

FIGURE 1 Mechanical model for description of viscoelastic properties of polymer in the transition zone.

sum of distortional $\Delta n_e(t)$ and orientational $\Delta n_s(t)$ contributions:

$$\Delta n(t) = \Delta n_e(t) + \Delta n_s(t) \tag{1}$$

On the basis of submolecule theory Read has shown,[14] that Bruster's law must hold also for non-equilibrium state with the same stress-optical coefficient as for equilibrium one. This is the basis for statement that

$$\Delta n_s(t) = C_s \sigma_s(t) \tag{2}$$

If it is assumed that similar situation is valid for the distortional component of birefringence as well, i.e. that

$$\Delta n_e(t) = C_e \sigma_e(t) \tag{3}$$

then the formula (1) may be rewritten as:

$$\Delta n(t) = C_e \sigma_e(t) + C_s \sigma_s(t) \tag{4}$$

where

$$C_s = C_\infty - C_e = \frac{2\pi}{45kT} \frac{(\bar{n}^2+2)^2}{\bar{n}} (\alpha_1 - \alpha_2) \tag{5}$$

is the stress-optical constant according to the rubber-like elasticity theory, C_e and C_∞ are Bruster's coefficients in the glass-like and equilibrium rubber-like state, $\bar{n}$ is the mean value of birefringence index, $\alpha_1 - \alpha_2$ is the optical anisotropy of the statistical chain segment, K is Boltzmann's constant and T is the absolute test temperature.

It follows from the model that $\sigma_e(t) = \sigma(t)$. Then by dividing Eq. (4) by $\sigma(t)$ gives:

$$C(t) = C_e + C_s \frac{\sigma_s(t)}{\sigma(t)}, \tag{6}$$

where $C(t)$ is the non-equilibrium Bruster's coefficient.

We assume that $\sigma_s(t) = E_s(t)\mathscr{E}$ and $\sigma(t) = E(t)\mathscr{E}$, where $\mathscr{E}$ is the relative strain.

Then Eq. (6) may be written in the following form:

$$C(t) = C_e + C_s \frac{E_s(t)}{E(t)} \tag{7}$$

hence

$$E_s(t) = \frac{C(t) - C_e}{C_s} E(t) \tag{8}$$

According to the accepted model the energy component of stress and, consequently, the distortional component of birefringence are present at all the stages of the equilibrium setting. Thus at the equilibrium $C_\infty = C_s + C_e$. C_s and C_e correlation is different for various polymers. For most polymers, however, C_s exceeds C_e in the absolute value by approximately two orders. In these cases it may be considered that $C_\infty = C_s$.

It follows from the above mentioned discussion that one needs to include some corrections into the principle of the time-temperature reduction, namely: a correction for the kinetic factor has to be introduced not for the entire non-equilibrium modulus $E(t)$ (as it is usually done) but only for its entropy component $E_s(t)$. That's why $E(t)$ value reduced to T_0 temperature will be:

$$E(t, T_0) = E(t, T) - E_s(t, T) + \frac{T_0 E_s(t, T)}{T} \tag{9}$$

The similar situation arises at time-temperature reduction of $C(t)$. Let's consider this case.

We assume that $C(t)$, $\sigma(t)$ and $\sigma_s(t)$ are related to the same stage of the equilibrium setting. As C_e doesn't depend on temperature, then according to the expression (6) we can write for T_0 and T:

$$C(t, T_0) = C_e + C_s(T_0) \frac{\sigma_s(t, T_0)}{\sigma(t, T)} \tag{10}$$

and

$$C(t, T_0) = C_e + C_s(T) \frac{\sigma_s(t, T)}{\sigma(t, T)} \tag{11}$$

Since a correction for the kinetic factor is necessary to introduce only for the entropy component: $\sigma_s(t, T_0) = (T_0/T)\sigma_s(t, T)$, then the difference $\sigma(t, T) - \sigma_s(t, T)$ should be considered independent of temperature. Then, taking into account that $C_s(T_0) = C_\infty(T_0) - C_e$ and $C_s(T) = C_\infty(T) - C_e$, we obtain the following equation:

$$\frac{C(t, T_0) - C_e}{C(t, T) - C_e} = \left[\frac{C_\infty(T_0) - C_e}{C_\infty(T) - C_e}\right] \frac{T_0}{T} \frac{\sigma(t, T)}{\sigma(t, T) - \sigma_s(t, T) + (T_0/T)\sigma_s(t, T)} \tag{12}$$

Hence we find the relation for reducing the Bruster's coefficient to T_0 temperature:

$$C(t, T_0) = C_e + [C(t, T) - C_e]\left[\frac{C_\infty(T_0) - C_e}{C_\infty(T) - C_e}\right]\frac{T_0}{T}\frac{\sigma(t, T_0)}{\sigma(t, T) - \sigma_s(t, T) + (T_0/T)\sigma_s(t, T)} \quad (13)$$

Finally by dividing the nominator and denominator in the right hand side of (13) by $\mathscr{E}$ we obtain:

$$C(t, T_0) = C_e + [C(t, T) - C_e]\left[\frac{C_\infty(T_0) - C_e}{C_\infty(T) - C_e}\right]\frac{T_0}{T}\frac{E(t, T)}{E(t, T) - E_s(t, T) + (T_0/T)E_s(t, T)} \quad (14)$$

The formulae (8), (9) and (14) were used in the present paper to calculate $E(t, T_0)$, $E_s(t, T_0)$ and $C(t, T_0)$ from the experimental data on the non-equilibrium photoelasticity of rubber.

EXPERIMENTAL

Transparent peroxide cured butadiene-acrylonitrile rubber (SKN-40) in the form of ~1 mm thick sheets was used for studies.

Combined stress relaxation and birefringence measurements in stretched rubber samples were made in the temperature range from -26.4 to 25°C and observation time range from 0.4 to 1000 sec by means of a mechanical-optical relaxometer whose diagram is shown in Figure 2.

Dumb-bell test pieces, 3.5 mm wide and 30 mm in operating part length, were subjected to stretching.

Test samples conditioning in a thermostat during the experiment was carried out with an accuracy up to ± 0.1°C in the thermocryogenic chamber of the relaxometer, provided with multilayer glass windows for the optical measurements.

The samples were stretched by a steel spring (see Figure 2). Time of stretching varied depending on the preset strain and temperature in the range from 0.05 to 0.1 sec.

Stress in a sample was recorded by means of a stiff dynamometer and tensometric circuit whose elements were connected in the following sequence: strain gauge bridge, direct current amplifier and loop oscillograph.

The measurement of sample strain was performed by cathetometer according to the marks plotted on the operating part of the dumb-bells. Rubber deformation, $\mathscr{E}$, changed depending on the test temperature in the range from 1.5 to 30%.

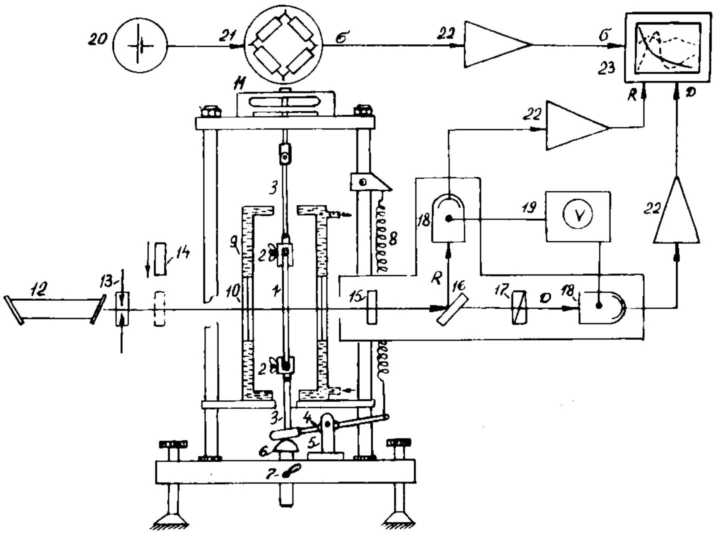

FIGURE 2 Mechanical-optical relaxometer: 1—test piece; 2—clamp; 3—traction; 4—lever; 5—post; 6—rod; 7—rod set screw; 8—steel spring; 9—thermocryogenic-chamber; 10—glass window; 11—dynamometer; 12—lazer; 13—iris; 14—quartz plate $\lambda_0/4$; 15—interference light filter; 16—glass plate; 17—analyzer; 18—photomultiplier tube; 19—high-voltage source; 20—dry cell; 21—strain gauge bridge; 22—amplifier; 23—loop oscillograph.

$E(t)$ values were calculated according to the formula:

$$E(t) = \frac{\sigma(t)\lambda}{\lambda - 1} \tag{15}$$

where $\sigma(t)$ is the stress calculated per cross-section of an unstrained sample; $\lambda = (1+\mathscr{E})$ is the extension ratio, equal to the ratio of the stretched sample length to the initial one.

The $E(t)$ values of rubber were within the limits of the linear viscoelastic behaviour of the material.

The elements in the optical scheme of the relaxometer were positioned in the following sequence: a gas He–Ne laser with light wave length $\lambda_0 = 632.8$ nm, iris, interference light filter, glass plate and an analyzer (see Figure 2). The glass plate was positioned at a 45° angle to the light beam and the extension axis of the sample was used for shaping a reference light beam in order to exclude intensity fluctuations in the light source and optical density changes in the sample during the experiment when calculating the birefringence value.

The intensity of light after passing through the plate and analyzer (D) and reflecting from plate (R) were recorded by means of the photoelectric circuit, whose elements were connected in the following sequence: a photomultiplier tube, a direct current amplifier and loop oscillograph.

Let us briefly consider an experimental method for birefringence measurement used in the present work.

When passing through a stretched polymer sample the plane polarized light wave is decomposed into components with amplitude A and phase difference δ: $A \operatorname{Cos} \omega t$ and $A \operatorname{Cos}(\omega t-\delta)$.

Hence, using the known Frenel's formulae for the polarized light the R and D values may be represented in the form

$$R = A^2 tg^2(\varphi-\chi)\frac{\cos^2(\varphi+\chi)+\cos^2(\varphi-\chi)}{\sin^2(\varphi+\chi)} \tag{16}$$

and

$$D = 2A^2 \frac{\cos^2\varphi \sin^2\chi}{\sin^2(\varphi+\chi)\cos(\varphi-\chi)}\left[\frac{\sin^4(\varphi/2-\chi/2)}{\cos(\varphi-\chi)}+\sin^2\frac{\delta}{2}\right] \tag{17}$$

where φ is the incidence angle of rays on the plate and χ is the refraction angle. The φ and χ values are interconnected by relationship:

$$\sin\varphi = n_0 \sin\chi \tag{18}$$

where n_0 is the refraction index of the plate material.

Expression (17) is convenient to write in a simple form:

$$D = D_0\left(B+\sin^2\frac{\delta}{2}\right) \tag{19}$$

When $\varphi = 45^\circ$ and $n_0 \simeq 1.52$ then $B = 5.4\times10^{-4}$ (i.e. $B = 1$) and the formula (19) is reduced to the expression

$$D \approx D_0 \sin^2\frac{\delta}{2} \tag{20}$$

This relation is valid only under the conditions of the constant optical density of the sample and constant incident light intensity, while the D/R ratio doesn't depend on these factors and is determined only by δ value. Hence it follows that

$$\frac{D}{R} \approx \frac{D_0}{R_0}\sin^2\frac{\delta}{2} \tag{21}$$

where D_0 and R_0 are the values of the corresponding intensities at a time moment when $\sin^2\delta/2 = 1$.

Thus the value of δ was found from the following equation:

$$\sin^2\frac{\delta}{2} \approx \frac{DR_0}{DR_0} \tag{22}$$

The non-equilibrium birefringence in the sample was calculated by the following formula:

$$\Delta n(t) = \frac{\delta\lambda_0\sqrt{\lambda}}{2\pi d_0} \tag{23}$$

where d_0 is the underformed sample thickness. The sign of $\Delta n(t)$ was found by means of a quartz plate $\lambda_0/4$, placed into the light beam in front of the sample (see Figure 2).

The positive $\Delta n(t)$ values for both glass-like and rubber-like states were observed in butadiene-acrylonitrile vulcanizate under discussion.

In accordance with Bruster's law the values of the non-equilibrium stress-optical coefficient were calculated by the formula:

$$C(t) = \frac{\Delta n(t)}{\sigma(t)\lambda} \tag{24}$$

The temperature dependence of the Bruster's equilibrium coefficient C_∞ of the butadiene-acrylonitrile vulcanizate was determined in the following manner. Equilibrium values $\Delta n(t)$ and $\sigma(t)$ were measured for a rubber sample, stretched to $\lambda = 1.5$ at 25°C. Then the stretched sample was subjected to slow cooling. During this process $\Delta n(t)$, $\sigma(t)$ and λ were measured at appropriate temperatures. The values of C_∞ were calculated from formula (24).

Temperature dependence of butadiene-acrylonitrile vulcanizate is shown in Figure 3. An abrupt decrease of C_∞ in the low temperature range is caused by the glass-transition of the vulcanizate.

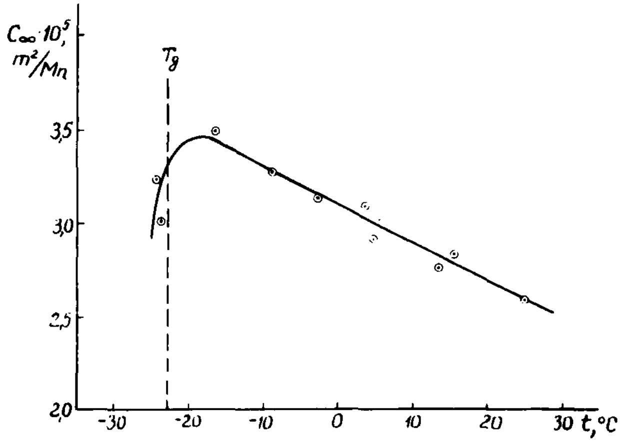

FIGURE 3 Temperature dependence of equilibrium stress-optical coefficient C_∞ for butadiene-acrylonitrile vulcanizate at $\lambda = 1.5$. Glass transition temperature (T_g) of butadiene-acrylonitrile rubber is shown by dashed line.

As in accordance with the linear dilatometry data glass transition temperature of butadiene-acrylonitrile rubber is $-23°C$, then $C_e = 3.34\ 10^{-7}$ m^2/Mn was found for the vulcanizate by means of the combined $\Delta n(t)$, $\sigma(t)$ and λ measurement at $-58°C$ under the conditions of step-wise stretching of the sample.

$C_{\infty} = 2.60\ 10^{-5}$ m^2/Mn at 25°C was found for the butadiene-acrylonitrile vulcanizate in a similar way.

RESULTS AND DISCUSSION

Time dependences $E(t)$ and $C(t)$ for the butadiene-acrylonitrile vulcanizate at various temperatures are shown in Figures 4 and 5. On the basis of these data the values of $E(t, T_0)$, $E_s(t, T_0)$, $E_e(t, T_0) = E(t, T_0) - E_s(t, T_0)$ and $C(t, T_0)$ were calculated according to the formulae (8), (9) and (14). Then using known procedure[7] we have plotted their master curves versus t/a_T, reduced to 25°C (a_T is a shift factor). These curves, shown in Figures 6 and 7, cover about 14 decimal orders of time. As can be seen in Figure 7, in the range of long observation times, rubber elasticity is actually of completely entropy nature but at the short times it is completely an energy one. In the middle part of the transition zone $E_s(t)$ and $E(t) - E_s(t)$ are comparable and elasticity is of a mixed character.

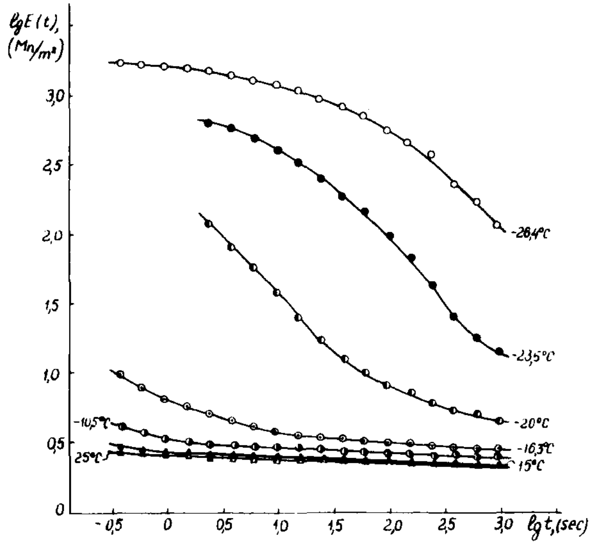

FIGURE 4 Time dependences of relaxation modulus $E(t)$ for butadiene-acrylonitrile vulcanizate at different temperatures.

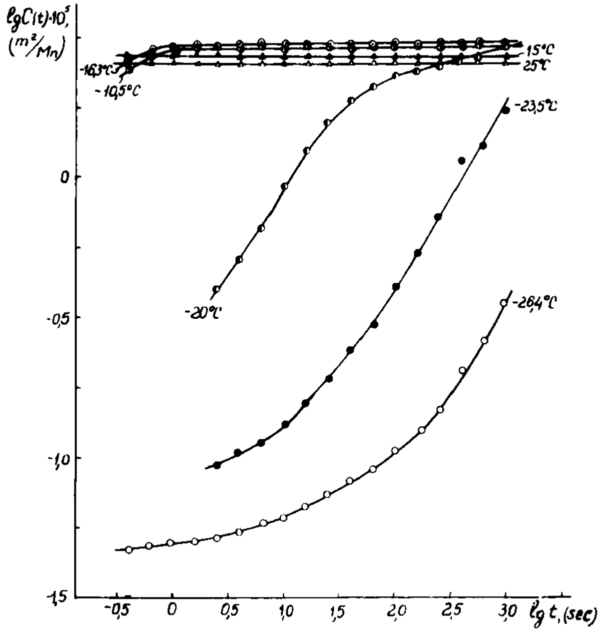

FIGURE 5 Time dependences of non-equilibrium stress-optical coefficient $C(t)$ for butadiene-acrylonitrile vulcanizate at different temperatures.

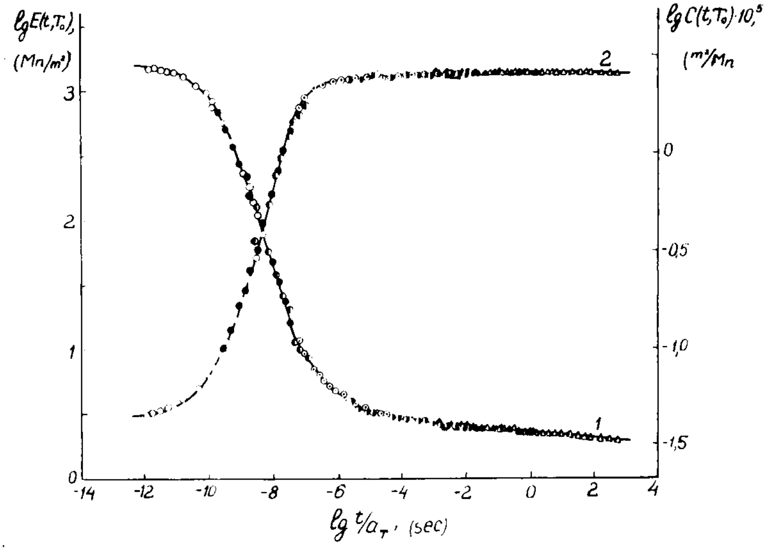

FIGURE 6 Reduced master curves of relaxation modulus $E(t, T_0)$ and non-equilibrium stress-optical coefficient $C(t, T_0)$ for butadiene-acrylonitrile vulcanizate at $T_0 = 298°K$: $1 - E(t, T_0)$, $2 - C(t, T_0)$.

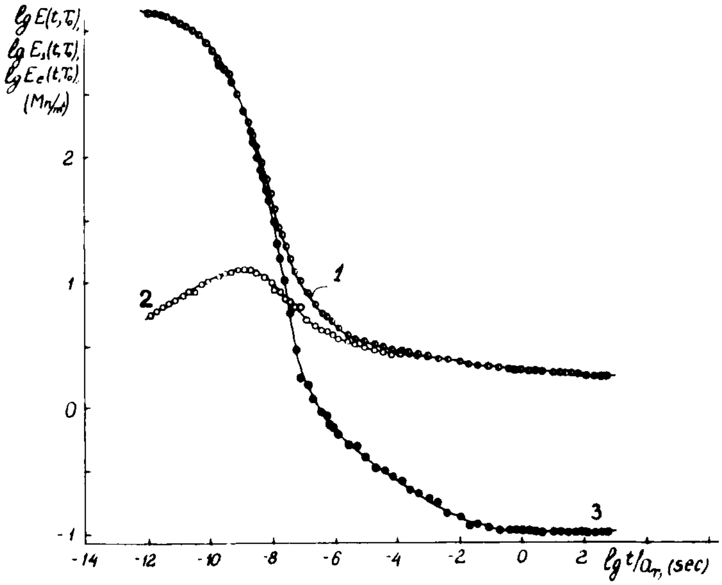

FIGURE 7 Reduced master curves of $E(t, T_0)$, $E_s(t, T_0)$ and $E_e(t, T_0) = E(t, T_0) - E_s(t, T_0)$ for butadiene-acrylonitrile vulcanizate at $T_0 = 298°K$: $1 - E(t, T_0)$; $2 - E_s(t, T_0)$; $3 - E_e(t, T_0)$.

While passing into the range of short times $E_s(t)$ increases and reaches maximum the value of 12.7 Mn/m^2. This value is about one order less than the maximum value estimate, $E_s(t) = 100$ Mn/m^2, made in the work.[12] At least two reasons of such difference may be indicated. Firstly, the estimate was made for polyethylene having the shortest size of the minimum chain segment, capable of the conformational changes. In the case of butadiene-acrylinitrile rubber the sizes of corresponding chain segments are larger and this must lead to the decrease in the presented estimate. Secondly, the estimate given in the work[12] was made on the assumption that distribution of chain conformations deviates as much as possible from the equilibrium one. At the same time it is clear that such a state is actually not feasible. This statement is confirmed by the study of the relaxation processes mechanism in the transition zone. The stress entropy component, arising during the relaxation process of the energy component begins to relax at once. That's why the maximum value of $E_s(t)$ is determined by the conditions when, due to these factors, the increasing and decreasing entropy velocities are equalized. Naturally, because of this the maximum value of $E_s(t)$ must be significantly lower as compared with the estimate made when these factors are neglected. Thus the result obtained should not be considered contradictory to the theory.

From the data, given in Figure 7 time relaxation spectra, $H(\tau)$ and $H_s(\tau)$,

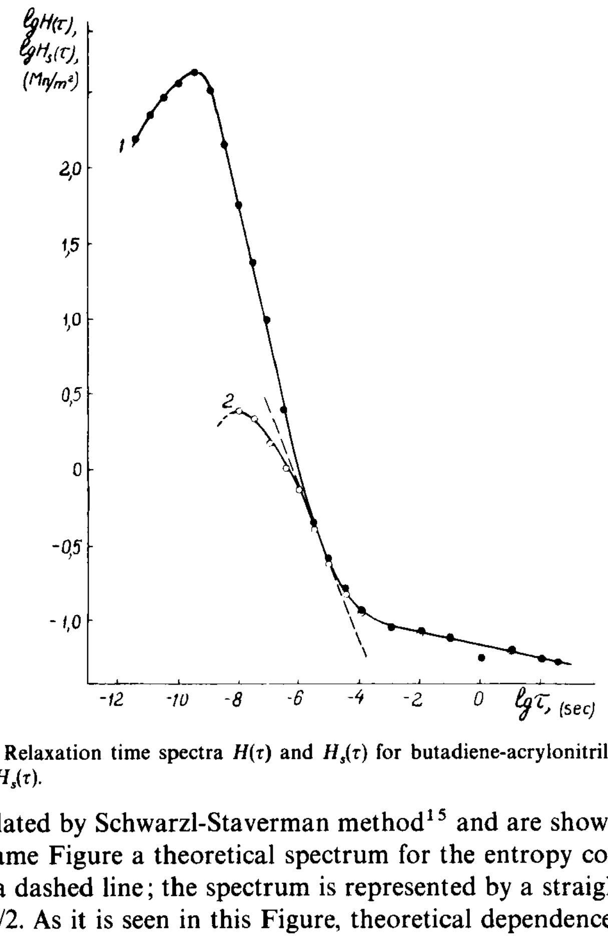

FIGURE 8 Relaxation time spectra $H(\tau)$ and $H_s(\tau)$ for butadiene-acrylonitrile vulcanizate: $1-H(\tau)$; $2-H_s(\tau)$.

were calculated by Schwarzl-Staverman method[15] and are shown in Figure 8. In the same Figure a theoretical spectrum for the entropy component is shown by a dashed line; the spectrum is represented by a straight line with a slope $-1/2$. As it is seen in this Figure, theoretical dependence is in good agreement with the spectrum of entropy component, obtained experimentally.

The above experimental data show, that relaxation of the entropy stress component defines the shape of spectrum only in a comparatively small part of the transition zone. The range of applicability for all the theories of viscoelastic properties proceeding from the purely entropy nature of elasticity is limited only by this part of the transition zone. The theoretical description of relaxation processes in the entire transition zone requires a combined study of both elasticity mechanisms.

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