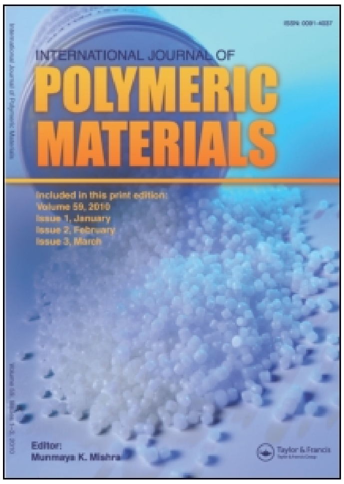

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Influence of Change of Relaxation Properties on Polymer Tensile Strength

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A specific property of polymer materials—the capability of the chain micromolecules to change shape due to external forces—manifests itself at the final polymer fracture stage (division into parts) in that its structure differs significantly, as a rule, from the initial stage. The description of such processes should take into account not only the change in the structure, but also change in the relaxation characteristics of the material associated with it. The present paper is a review of the state of the problem and describes the means for determining the relaxation characteristics of polymer materials at the final fracture stage.

KEY WORDS Tensile strength, relaxation times, reaction kinetics.

1. SPECIFIC REGULARITIES OF HIGH-POLYMER FRACTURE

Virtually all the most important polymer properties are relaxation. The peculiarities of the relaxation properties of polymer materials are due to the variety of kinetic units.

Therefore, the description of the relaxation behavior of such materials requires, as a rule, using the concept of "range of relaxation times."[1] Links, segments, macromolecular parts, whole molecules, supramolecular formations, crystallites, etc. can serve as the kinetic units participating in the various relaxation processes. The large body of information about the relaxation phenomena, kinetic processes of the relaxation nature, and the interrelation between the mobility and structure of the polymers are discussed in a number of monographs and reviews.[1-7]

However, in a great number of cases, such as in References 8–10, the relaxation processes of the structural rearrangement due to the deforming forces at the strain stages do not take into full account the stage of polymer material division.

Information about the nature of the kinetic units participating in any relaxation process of polymer material deformation can be obtained by qualitative estimation of the change in the range of the relaxation time or lag time. The change in the molecular shape which occurs in a general form as a result of polymer strain determines not only the change in the structure, but also the resistance of the material to strain and fracture. From this viewpoint, the influences of the polymer structure on the tensile strength and fatigue resistance should be studied by comparing the initial polymer structure not only, and sometimes not so extensively, with its initial relaxation property characteristics, but also with the structure and relaxation characteristics of the material at the final strain stage. This is especially important for describing such a relaxation process as polymer material fracture.

Polymer material fracture due to external mechanical forces was studied in the early 1950s[11] as a relaxation process, with the relaxation time a function of the applied stress. At the present time, a great deal of information has been gathered to reveal the variety of kinetic units participating in the fracture process.[12-16]

Thus, the numerous simultaneous relaxation processes, each of which is characterized by kinetic units and relaxation times, occur during strain and mechanical fracture of the polymers. The relaxation times are a function of the stress acting on the kinetic units. In real materials, we observe a heterogeneous distribution of the stresses over the volume of the body.[3,13,14,15] Therefore, at different points of the deforming polymer body the relaxation processes proceed at different rates. The most intensive rearrangement of the kinetic units takes place at the microdefect apices where the stress peaks are concentrated.

In light of the above-stated consideration, it is expedient to determine which bonds are ruptured in the elementary act of strain and fracture during the rearrangement of the polymer structure elements. If we disregard the mechanical-chemical processes accompanying the polymer strains,[17] it is necessary to take into account only the rupture of the bonds as the result of the intermolecular interaction forces in the process of polymer strain. It is more complicated to answer the question concerning the process of polymer body distribution. A number of works report that (Reference 13, p. 55) investigations of the polymer body fracture due to the uniaxial load were based on the mechanisms accompanying the rupture of the bonds due to the intermolecular interaction. An excellent example may be the plastic deformation preceding the rupture of the high-visco-elastic polymer systems. An alternative view-point is based on the chemical bond rupture conception formulated in a number of other works.[13,14,16,18-20] If we consider the process of mechanical fracture of crosslinked polymers, it is only natural that the division of the polymer body of such a structure is impossible without the rupture of the bonds caused by the main chemical valence forces. However, it is also necessary in this case to take account of the intermolecular interacting forces. The relation of the contribution to the resistance to the division of the forces of the first and second kinds depends on the load regime (Reference 15, p. 237). At low temperatures and high loading rates, when the rearrangement of the kinetic units is slow to provide the appropriate level of "dissipate" stresses and reinforcement at the expense of orientation of the macromolecular parts at the stresses' peaks, the determining factor is the rupture of the bonds by the main chemical valence forces. The initially strongly oriented polymeric bodies, such as fiber, are ruptured by this mechanism. In all other cases, the determining factor is the contribution of the intermolecular interacting forces.

The role of the intermolecular interaction in the polymer's resistance to fracture can be illustrated by comparing cured rubbers with an equal degree of cross-linking but different amounts of polar atomic groups in the chain. Naturally, the polymer

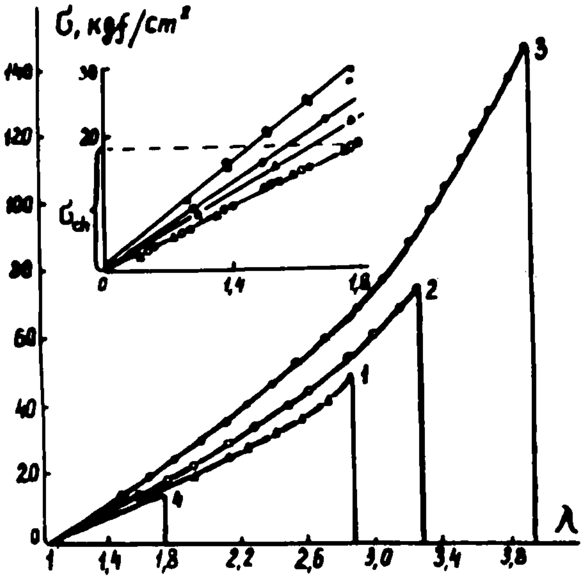

FIGURE 1 Stress-strain curve of vulcanized nitril rubbers with equal cross-linked density distinguished by the content of nitril groups in macromolecules 1 = 18%, 2 = 28%, and 3 = 40%.

containing a large number of polar atomic groups is characterized by a more intensive intermolecular interaction. Due to the effect of the external force and the heat energy fluctuation, the bonds eventually will break down. The stable bonds effected by the main chemical valence forces will resist polymer body division. Since the degree of the cross-linking is assumed to be similar, according to the experimental conditions, the resistance to fracture of such polymers, in terms of times sufficient for terminating the rearrangement processes of all the kinetic unit types, should also be similar. In Figure 1, curve 4 corresponds to the dependence $\sigma = f(\lambda)$, where σ is the stress, λ is the relative length l/l_0, provided that each value corresponds to σ value which is attained after the relaxation process is essentially complete. For such a quasi-equilibrium relation $\sigma = f(\lambda)$, the similar value for the destructive stress is typical of all three cured rubbers. This is not surprising, as only the main chemical valence forces react against the load at the final strain stage under such a deformation regime. The number of all the cured rubbers is the same, according to the experiment. Quite another picture is observed in the final strain rate. In this case, the higher the destructive stress value, the higher the concentration of the polar atomic arrangement in the chain. By comparing the destructive stress values obtained during the quasi-equilibrium means of deformation with the final rate strain, one can clearly see that those values differ by almost a whole order. This allows us to conclude that in case of a mechanical fracture of unoriented final rate polymers, the most significant contribution will come from the intermolecular interaction forces. This assertion is related to a case where the processes of rearrangement of the kinetic units are effected during the final strain rate process. If the polymer body undergoes a mechanical fracture whereby the rearrangement of the structural elements is considered to be insignificant, for example in pre-oriented polymers (fibers), or under conditions when the above-indicated rearrangement fails to take place, it obeys the general regularities typical both of polymeric and low-molecular substances (for example, References 6 and 18):

$$\tau_p = \tau_0 \exp \frac{U_0 - \gamma\sigma_r}{kT} \tag{1}$$

where τ_0 is the period of variation of the kinetic units, σ_r is the destructive stress, γ is the parameter of the equation reflecting the change in the structure of the polymer body during the fracture process, U_0 is the activation energy of the elementary act of fracture at $\sigma_r = 0$

The parameters of Equation (1) for all solid materials remain constant over a broad range of temperature and time for the destructive stress action τ_p. According to Equation (1), the logarithmic dependences $\ln \tau_p = f(1/T)$ and $\ln \tau_p = f'(\sigma_p)$ are approximated by a straight line, which allows one to conveniently predict the behavior of different bodies (including polymeric) over a broad range of temperature and time for the destructive stress action.

However, the above-stated advantages of the tensile strength Equation (1) are not evident when testing highly-elastic polymers. When Equation (1) was applied to elastomers, the equation parameter γ depended on both the experimental temperature and the level of the σ_r values. In the case of elastomer fracture, the destructive stress depends on the relation between the mobility of the kinetic units involved in the relaxation process of the mechanical fracture and the rate of the increasing general defect. The numerous experiments carried out on elastomers of different structures showed that σ_r and the rate of the increasing general defect v (determined with the aid of high-speed cinematography of the final stage of polymeric body fracture) are associated by a simple relation:

$$\sigma_r = K \cdot v \cdot \exp(E/RT) \tag{2}$$

(Reference 15, p. 229) following from the theory of absolute reaction rates by Eyring *et al.*

The rate of increase in the general defect v appeared to be related to the rate of displacement of the dynamometer clamp V by the dependence:

$$v \approx \text{const} \cdot V^n \tag{3}$$

where n depends on the mobility of the kinetic units involved in the fracture process. The pattern of fracture of soft cured rubbers is close to that of viscous flow of linear elastomers. The formulation of Equation (2) taking into account Equation (3) reminds us of the known Ostwald de-Vila equation approximating the viscous flow of the linear elastomers in the regime of rates where the macromolecule changes shape.

Thus, the specificity of the polymeric macromolecular structure manifests itself in the macromolecular flexibility as well as in the specific regularities of the fracture process.

In accordance with the above-mentioned analysis, the mechanical fracture of polymers is a relaxation process characterized by the variety of the kinetic units involved in it and the changing mobility of these units upon approaching the final fracture stage. With an increase in the degree of elastomer strain, the mobility of the kinetic units varies substantially. The situation becomes complicated in view of the fact that at this stage of sample strain, the material on the whole deforms differently at different points of the sample. Figure 2 displays the patterns of strain distribution in polymer samples observed prior to their fracture: a) in rubber (half

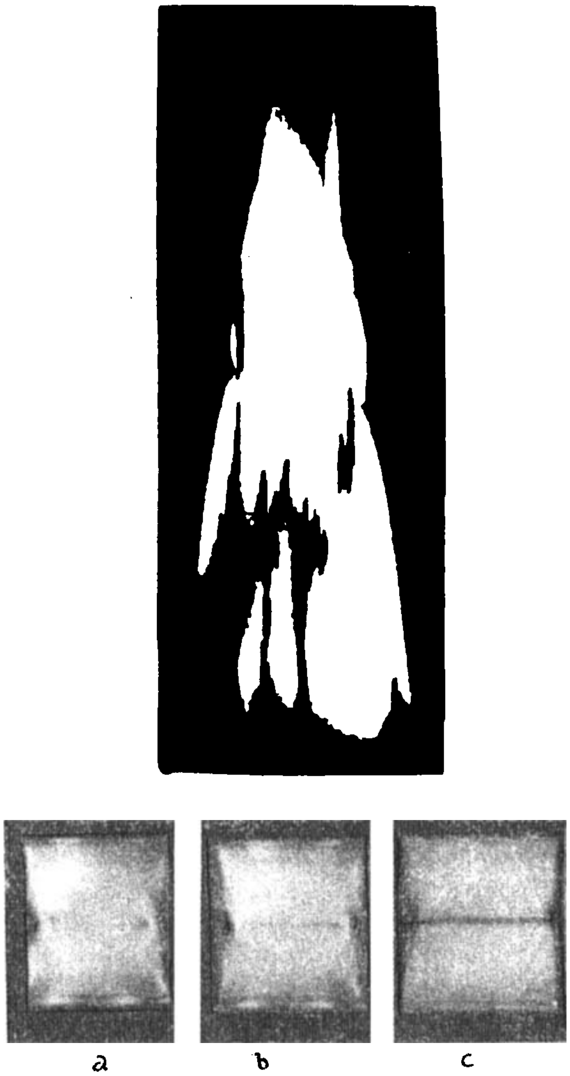

FIGURE 2 Cinefilm pictures of sample fracture: a) vulcanized film of natural rubber latex at 294°K; b) polymethylmethacrylate films at 293°K. Initial strain stage = *a* − *b*.

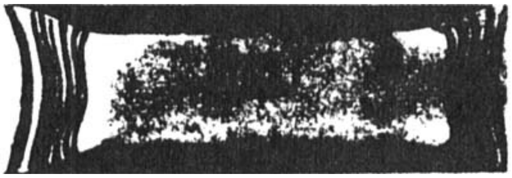

FIGURE 3 Cinefilm pictures of the final fracture stage of polyethyleneterephthalate at 313°K.

of the extended sample is illustrated), b) in a glass-like polyethyleneterephthalate. At temperature close to that of brittleness, there appears a surface corresponding to the largest stress values for the sample that is perpendicular to the direction of the external forces prior to division of the sample (Figure 3).

Figures 2 and 3 illustrate with cinefilm pictures in polarized light the strain and fracture of polymeric bodies in the ranges corresponding to brittle, forced-elastic and high-elastic fracture.

Examination of the high-speed cinefilms of polymer fracture under conditions corresponding to the above-mentioned states as well as the study and processing of these same cinefilms (Reference 15, p. 118) showed that the distribution of the local strains and stresses in the polymer samples were heterogeneous, depended on the fracture mechanism (e.g. brittle, forced-elastic), and changed continuously on approaching the final fracture stage (sample division).

In the case of polymeric bodies the macromolecules are capable of changing their shape by external forces, the smoothness of the contours of the increasing general defect is typical and, consequently, the same can be said of the stress peaks in the defect apices. The above-enumerated features of polymer fracture processes depend substantially on the mobility of the kinetic units, which change in the course of strain up to the moment of fracture. The polymeric body becomes stronger with strain. Additional orientation of the polymer material at the defect apices is appreciable. The more pronounced this process is, the higher the resistance of the polymeric body to fracture. The examination and processing of the polarized light cinefilms allow us to compare the material's ability toward additional orientation with its resistance to mechanical fracture. The birefringence of polystyrene is proportional to its high-elastic strain. After interpreting the polarized light cinefilms of polystyrene strain prior to fracture, we were able to determine the birefringence coefficients of the general defect apex and the coefficient of additional orientation in the mid-section of the sample:

$$\delta = \frac{\Delta n_{\text{def}}}{\Delta n},$$

where Δn_{def} and Δn are the birefringence at the defect apex and in the center of the sample.

Figure 4 illustrates the change with temperature of the coefficient of the additional orientation at the general defect apex of the polystyrene sample. The investigated temperature range can be divided into 3 parts: parts II and III correspond to the drastic decrease in the σ_r values. The σ_r values typical of both linear and cross-

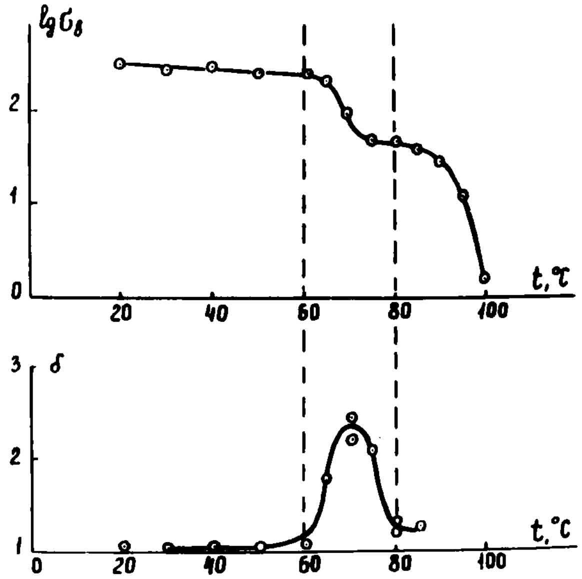

FIGURE 4 Temperature curves of the destructive stress and degree of additional orientation δ for polystyrene.

linked elastomers decrease differently with increasing temperature. The linear structure of polystyrene is due to an appreciable development of inelastic strains due to viscous flow when the corresponding temperatures are attained. The development of the inelastic deformations of linear polymers is accompanied by a decrease in the attained maximum δ values. The general tendency of the linear polymers toward a decrease in the σ_r values with a rise in temperature (in comparison with region III) weakens significantly the elastomers in region II, in which the kinetic units are "defrozen," causing the additional orientation, and in which a rise in δ with increasing temperature is observed. A further decrease in the δ values, related to the development of inelastic strains[21] will not occur as a result of cross-linking of macromolecules at the expense of the main chemical valences. In this case, the value remains constant at temperatures where the polymeric body can fully realize additional orientation; meanwhile the characteristics of the tensile strength decrease with rising temperature due to the increase in intensity of the fluctuation of the heat energy.

Figure 5 illustrates the dependences $\sigma_r = f(T)$ and $\delta = f'(T)$ for cross-linked rubbers. In region III, the additional orientation of cross-linked rubbers is effected completely and the δ value does not change with increasing temperature. In region II, the additional orientation value increases with temperature. This is natural, since with a rise in temperature the mobility of the kinetic units increases, and the higher the temperature, the higher the degree of "strengthening further" the material at the section where the general defect develops. These particular features of structural changes in the polymeric material during the process of its strain prior to fracture influence appreciably the characteristics of its tensile strength. Figure 5 demonstrates the dependence between the destructive stress values and the tem-

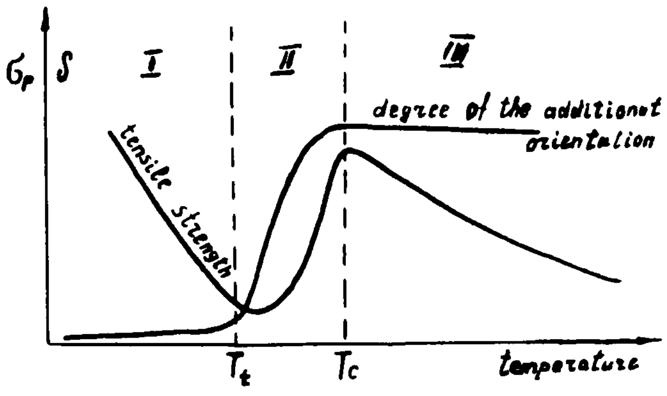

FIGURE 5 Temperature curves of destructive stress σ_r and degree of additional orientation of cross-linked elastomers δ.

perature. In those temperature regions where no significant change in the structure related to the rearrangement of the macromolecule particles takes place, the general tendency is for the values of the tensile strength characteristics to decrease with a rise in temperature, following, for example, from Equation (2). In temperature region II, where the polymeric body is capable of rearranging its structure in the strain process prior to fracture, one observes a rise in the destructive stress values with a corresponding rise in temperature. The rise in values is due to the increase in the mobility of the kinetic units with a rise in temperature. The more mobile the kinetics are, the more the polymer becomes further "strengthened" in the strain process at the moment of fracture.

The non-monotonic change in the characteristics of the tensile strength of the elastomers with a change in temperature was observed in many experiments, in particular those related to finding the optimal dispersal conditions for shock-proof polymer articles so as to make them available for secondary usage.[22,23] It was shown[23] that the temperature dependence σ_r describes fairly well the equations reflecting the relaxation nature of the fracture process. The principle of the temperature-rate analog is observed within the limits of one fracture mechanism (within the limits of constancy of Equation (2) parameters, i.e. in the temperature (or rate) regions of the monotonic change in σ_r. The generalized curve was obtained from the displacement of the pre-extremal dependence sections $\sigma_r = f(T)$.[23] In this case, the dependence of the reduction factor on temperature was fairly satisfied by the Williams-Landel-Ferri equation with constant coefficients.

In the temperature region where a rise in the σ_r values is observed with increasing temperatures, the Equation (2) and (3) parameters, in particular n, are temperature dependent. When such conditions prevail at the final fracture stage, we can observe not only an appreciable rearrangement of the polymer structure, but also a substantial change in the relaxation times spectrum associated with this rearrangement. In this case, no matter which bonds undergo rupture (due to the forces of the main chemical valences or the intermolecular interaction ö) in the course of the relaxation process, the elementary set of such a process can be presented as a chemical reaction, wherein the primarily whole elementary volume is divided into two parts:

$$X_2 + \Omega = 2X \tag{4}$$

where X is the bulk of the substance related to one of the two surfaces formed as a result of an elementary set of fracture: Ω is the portion of energy necessary for effecting this act. Here, in this act, the structural fragments serve as the kinetic units. These fragments are included in the elementary fracture volume (EFV) wherein the potential energy storage increases while the sample is being loaded. Depending on the polymer structure and its relaxation properties, the arriving energy is distributed irregularly. It localizes mainly at the micro-defect apices. When the quantity of the energy is sufficient to overcome the potential barrier, the elementary fracture takes place. In the course of this act, part of the energy which accumulated in EFV during the strain process passes into the surface energy generated by the process. This act is accompanied by the rupture of the bonds providing the continuity of the material. In case of fracture of the polymeric body pre-oriented in the direction of the external forces, the bonds are ruptured by the main chemical valences forces.[6,14]

Irrespective of the type of bonds ruptured in the elementary set, the displacement of the elementary volumes due to external stress is irreversible and similar to the irreversible displacement of the macromolecule segments during the flow of the viscoelastic polymer sample. In our opinion, the principal distinction is in the type of the kinetic units participating in the elementary act of these processes. When a polymer in a high-elastic state is ruptured, the relaxation characteristics and type of kinetic units undergo an appreciable change in comparison with the initial strain stages.

The mechanisms for the irreversible changes occurring during the elementary fracture process and the viscous flow of rubbers are actually the same. It should be noted that both processes are approximated by an expression of the same form. In a narrow strain rate range it is known that the viscous flow of the polymers is approximated by the Ostwald de-Vila power law. According to this law, the stress is related to the shear rate by a power dependence similar to that coupling the destructive stress and strain rate in Equations (2) and (3). It is necessary to determine the bounds of applicability of Equation (2). It is argued (Reference 16, p. 187) that Equations (2) and (3) describe the fracture of the polymer wherein the molecular mobility of the polymer chains is high; it is also believed that these equations are not applicable to glass-like state polymers. The latter case is accepted here if taken to mean the fracture mechanism of the glass-like body whereas the macromolecules are capable of changing their shape by the external forces. But taking into account that the forced highly-elastic polymer manifests itself primarily in the glassy state, we should limit application of Equations (2) and (3) to the region where the macromolecules are capable of changing shape under the action of external forces. Under such conditions, the law of polymer fracture should distinguish itself clearly from the fracture laws applicable to nonpolymeric systems. This also includes polymers under conditions at which they are capable of changing the shape of the macromolecules under the action of external forces. This is important to bear in mind when the samples are being prepared for experiment. As was stated above, the polymeric and non-polymeric bodies (as was qualified above) obey the dependences (1). However the investigation[16] of durability carried out with different elastomers showed that the temperature-time dependence of the tensile strength is described by the equation in the following form:

$$\sigma_r = C \cdot \sigma_r^{-b} \tag{5}$$

where C and b are the equation parameters. Equation (5) can assume the following form:

$$\sigma_r = A \cdot V^{1/m} \cdot \exp(U'/mKT) \tag{6}$$

where Equations (2), (3) and (5) are identical, at $m = 1 + b$.

2. METHODS FOR ESTIMATING THE CHANGE IN THE CHARACTER OF THE KINETIC UNITS AND THE SPECTRA OF THE MOLECULAR RELAXATION TIMES IN THE PROCESS OF POLYMER STRAIN AT THE MOMENT OF FRACTURE

The above-considered continuous change in the nature of the kinetic units and their mobility in the processes of strain and fracture of polymers can be characterized by following the change in the bulk wherein the elementary act of the process takes place, and the change in the range of the relaxation times. Taking into account the above-mentioned nonuniform distribution of the body volume characteristics under consideration, it is reasonable to relate the characteristics under study to macro-volumes at the apex of the general defect.

With this aim in view, two solutions (most effective) to the problem can be suggested. The first one boils down to determining the range of relaxation times or lag times by the traditional methods at different strain stages. Then, the observed change in relaxation characteristics should be extrapolated to strain values corresponding to the division of the body. We can determine the magnitudes of the kinetic units using the Alexandrov-Gurevich relation:

$$\tau = \tau_0 \exp\left(\frac{U - \gamma\sigma}{kT}\right) \tag{7}$$

where τ is the relaxation time, $\gamma = \alpha \cdot \beta$, α is the elementary volume, β is (in our examples) the overstress coefficient for the defect apex.

The second method for solving the problem is estimating the rate of spontaneous contraction of the polymer taken to be in a high-elastic state at the moment of division of the sample. This method makes use of high-speed cinematography of the final elastomer fracture stage. The first such attempts[24] were made in 1960.

The application of high-speed cinematography is of principal significance, as it excludes the influence of the inertia of the recording device. The synchronization of the moment of sample division and triggering of the high-speed cinecamers[25] afford abundant information related to the spontaneous contraction of the elastomers at the moment of division.[26,27]

From the analysis of the range of relaxation times of cured rubbers obtained at the final fracture stage, it follows that under the experimental conditions (294°K, extension rate 550 mm/min) the cured rubbers are not glass-like, but are in a high-elastic state.

The analysis of the two independent methods has shown that although the processing of the data on relaxation of stresses at different magnitudes of strain provides information concerning both the changes in the kinetic process of re-arrangement of the structure elements and the changes in the intensity of the chemical and intermolecular interaction, that method has a number of definite shortcomings. They consist in the fact that in the process of stress relaxation (as well as in the case of creepage; see, for example[10]) two opposing forces prevent the contraction of the polymer on each section of the macromolecule confined within the neighboring nodes of the spatial network. On the other hand, when the sample undergoes division, no external force prevents the contraction of its parts formed during fracture. Therefore the spontaneous contraction affords more valid information about the relaxation characteristics of the polymer at the final stage of rupture than does the stress relaxation. Figure 6 illustrates the cinegrams of the final strain stage of a cured butadiennitrilacrylic rubber containing 28% nitrilacrylate component. Investigations of the time dependence of the rate of spontaneous contraction (SC) during the fracture of the elastomer[24] showed that as a result of the acting inertial forces, an oscillatory process is added to the process of spontaneous contraction during elastomer fracture. Although the equation for describing the

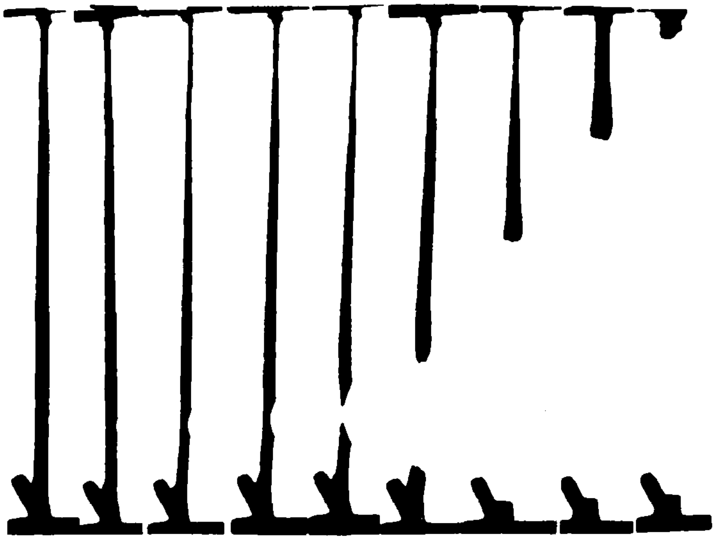

FIGURE 6 Subsequent stages of fracture of vulcanized rubber SKN-26 (cinegram).

spontaneous contraction for the elastomer using only one relaxation time is formally identical to the stress relaxation equation,[29] the approximation of the spontaneous contraction, taking into account the oscillatory processes, assumes the following form:

$$I_t = K\cdot(1 - A_1^2\cdot A_2^2)^{1/2}\cdot\exp(-t/A_2)\cdot\sin[A_1\cdot t + \arctan(A_1\cdot A_2)] \qquad (8)$$

where K_1A_1, A_2 are the approximation coefficients, I_z is the compliance during SC; $I_t = \varepsilon_t/\sigma_0$, where ε_t is the instantaneous strain during SC; σ_0 is the initial stress, i.e. at the time of fracture of the sample. Equation (8) can be presented as follows:

$$I_t = K_1\cdot\exp(-t/A_2)\cdot\sin(A_1t + C) \qquad (9)$$

The analysis of the experimental data[29] has shown that the parameter C and the ratio of parameters K_1/K are not dependent on the degree of extension λ_0; the mean values $C_{\text{aver}} = 0.78$; $K_1/K_{\text{aver}} = 1.41$.

From Equations (8) and (9) it follows that $C = \arctan(A_1\cdot A_2)$, $K_1/K = (1 + A_1^2\cdot A_2^2)^{1/2}$. The product of the $A_1\cdot A_2$ parameters found from the mean values of C and K_1/K equals unity. The product $A_1\cdot A_2$ for different λ_0 values determined from the experimental data approximated unity. The physical significance of parameter A_2 is the lag time during the spontaneous contraction; parameter A_1 is the oscillation frequency during the spontaneous contraction of the ruptured elastomer parts. The approximation results of the experimental spontaneous contraction of the ruptured elastomer showed that the oscillation of the sample during SC over the broad range of λ_0 occurs at a frequency qualitatively equal to the inverse value of the lag time. The observed rise in θ ($\theta = A_2$ is the lag time) was associated[29] with the orientation of the elastomer chain sections as the extension increased. The possibility of describing SC at λ_0 = const by one lag time implies that in the course of transition from the initial, small-deformed state to the final ruptured state, one can observe a "cut" in the spectra of the relaxation time responsible for the conformation displacement of the molecular lengths. Comparison of the elementary data obtained from the dependence of the polymer relaxation characteristics on the degree of extension and the θ values of the corresponding strain during the sample division has shown that the qualitative character of the observed dependences coincide. However, the absolute values for the relaxation and lag times are distinct from one another. As was shown above, this is due to different conditions of the on-going relaxation process and the spontaneous contraction process.

The fact that the characteristics of the relaxation processes of the polymer structure re-arrangement change in the course of its strain prior to fracture confirmed that the polymer with relaxation characteristics different from those which can be obtained from an unruptured polymer is ruptured. The changes in the relaxation characteristics of the polymer material which occur during its strain prior to fracture should be taken into account when reprocessing, modifying, and operating with polymeric systems.

It is only natural that the manufacturers of polymeric articles who are striving to raise productivity are often confined to discontinuity of the material. This discontinuity develops when definite strain rates are attained (Reference 3, p. 189). The relaxation nature of this phenomenon necessitates controlling them by means of a directed change in the relaxation times at the final (fracturing) stages of this process.

Polymeric articles gradually lose their primary properties after a period of service. The critical service characteristics deteriorate drastically as a result of repeated strains. The work used for strain is partially spent to increase the heat storage in the deformed body and to activate the chemical processes, leading to the degradation of the polymeric material. The share of the mechanical loss spent for activating the chemical processes occurring during multiple strains is determined by the internal friction in the system. The increase in the mobility of the kinetic elements and simultaneous decrease in the internal friction can essentially influence the resistance to fatigue arising from multiple strains of the polymer material. In this case, however it is necessary to take into account that the increase in the mobility of the kinetic units at the expense of an introduced plasticizer can simultaneously significantly decrease the value for the initial characteristics of the tensile strength, thus decreasing appreciably the resistance to fatigue. The rupturing elastomer stress value will increase or decrease depending on the concentration and nature of the plasticizer.[30] The change in the initial characteristics of the elastomer tensile strength influences substantially its resistance to fatigue. So, the number of cycles of multiple strains N which the material withstands prior to its fracture is related to the initial rupturing stress value by the following ratio[3,32]:

$$N = \frac{RT}{\Delta E} \cdot \ln(\sigma_r / \sigma_{\max}) \tag{10}$$

where σ_r is the initial rupturing stress value, determined from the strain rate corresponding to the rate of the multiple sample strain during its fatigue process; $\sigma_{\max}$ is the maximum value for the stress developing per strain cycle; ΔE is the change in the E value in Equation (2) taking place during one strain cycle (Reference 3, p. 290).

We have mentioned above that part of the hysteretic loss in each strain cycle is spent to activate the chemical processes caused by the degradation of the polymeric material. The comparison of the ΔE values with those of the ΔA hysterestic loss has shown a direct connection between the two magnitudes:

$$\Delta E = \Omega \cdot \Delta A \tag{11}$$

The coefficient Ω indicates the share of the hysteretic loss ΔA spent for jumping the potential barrier ΔE for one strain cycle.

The tensile strength of the material decreases during the multiple strain process. Each test cycle is characterized by a definite destructive stress value:

$$\sigma_{r1} > \sigma_{r2} > \sigma_{r3} \cdots > \sigma_{ri} \cdots$$

where σ_{r1} is the destructive stress value for the sample in the i-cycle.

The experiment has shown that the behavior of the samples under investigation for all the fatigue stages during cyclic loading is described by the temperature rate dependence,[2,3] and the parameter K and n do not change noticeably during the fatigue process.

Taking into account (according to the experiment with $N >> 10$) that in the cyclic test process $\Delta E = \text{const}$, the expression of the destructive stress value in the corresponding cycle will assume the following form:

$$\begin{aligned} \sigma_{r1} &= K_1 \cdot V^n \exp(E/RT) && \text{cycle one} \\ \sigma_{r2} &= K_1 \cdot V^n \exp\left(\frac{E - \Delta E}{RT}\right) && \text{cycle two} \\ \hline \sigma_{ri} &= K_1 \cdot V^n \exp\left(\frac{E - (i-1)\Delta E}{RT}\right) && \text{cycle } i \end{aligned} \tag{12}$$

The sample will fracture in case of a practical equality of the destructive stress values characterizing the sample tensile strength in the N cycle and the ultimately acting stress $\sigma_{\max}$ per cycle, i.e.

$$\sigma_{rN} \leqslant \sigma_{\max} \tag{13}$$

Let us consider the relation σ_{r1}/σ_{rN}. Using (12), we obtain

$$\frac{\sigma_{r1}}{\sigma_{rN}} = \frac{K_1 \cdot V^n \cdot \exp(E/RT)}{K_1 \cdot V^n \cdot \exp\left(\frac{E - (N-1)\Delta E}{RT}\right)} \tag{14}$$

Taking into account condition (13) and considering $N >> 1$, we obtain a dependence between the number of cycles which the sample will withstand prior to fracture and its initial tensile strength, maximum stress per strain cycle and value ΔE, depending on the magnitude of the hysteretic loss (11)

$$N = \frac{RT}{\Omega \cdot \Delta A} \cdot \ln(\sigma_r/\sigma_{\max}) \tag{15}$$

In this expression, the values Ω, ΔA, σ_{r1} and $\sigma_{\max}$ depend on the relaxation properties of the polymeric material. The values σ_{r1} and $\sigma_{\max}$, as we can see from above, are determined by the relaxation properties inherent in the sample at the final fracture stage.

The examples presented above are an indication of the practical significance for studying the relaxation properties of polymer materials at the final strain (fracture) stage. Naturally, the expounded considerations can be extended to examples associated with the adhesion fracture mechanism for polymer systems.

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