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Abstract

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ON THE LONG-TERM STRENGTH OF HIGHLY ELASTIC POLYMERS*

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The basic relation of S. N. Zhurkov' s theory of strength [1],

$$\tau = \tau_0 e^{(U_0 - \gamma\sigma)/kT}, \tag{1}$$

assumes an exponential dependence between the lifetime τ and the breaking stress under simple extension σ. In reality, however, for rubbers, for example, this dependence proves to be more complex and, as will be shown below, even nonmonotonic.

In relation (1): T is the absolute temperature; k is Boltzmann' s constant; τ_0 is a constant having the dimension of time and, in order of magnitude, close to the period of the natural vibrations of atoms; U_0 is the initial activation energy of the fracture process, which for highly oriented polymer materials has values close to the energy of the corresponding chemical bonds.

The coefficient γ, which characterizes the dependence of the effective value of the activation energy of the process on the magnitude of the applied stress, depends substantially on the structure of the material. In particular, it has been shown that the so-called strengthening achieved by drawing oriented polymers is associated with a decrease in γ [2].

In the works of S. N. Zhurkov, the parameter γ is assigned the physical meaning of a stress-concentration coefficient at defects present in real solids.

According to [3], the coefficient γ can be represented as the product

$$\gamma = \omega\beta, \tag{2}$$

where ω is the fluctuation volume, and β is a dimensionless coefficient of stress concentration near the most dangerous defect.

Since the purpose of the present work is to elucidate the possibility of extending the theory to highly elastic rupture, the most essential question is that of the dependence of the coefficient γ on deformation. In what follows, it is apparently necessary to keep in mind: 1) the purely geometric influence of deformation on

the stress-concentration coefficient near defects, and 2) the orientational effect leading to a change in the structure of the material [4].

For an approximate consideration, we shall use the known relation from the theory of elasticity for the stress-concentration coefficient near an elliptical hole, one of whose axes coincides in direction with the tensile force.

The corresponding expression has the form [5]:

$$\beta' = 1 + 2b/a, \tag{3}$$

where a and b characterize the dimensions of the hole along the axes of the ellipse, respectively along and transverse to the direction of action of the tensile force.

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* K. N. Lazareva took part in the work.

Upon stretching the specimen, the hole is deformed in such a way that the ratio b/a decreases.

From the condition of constancy of volume during deformation, the following dependence of β' on the degree of extension (λ) follows:

$$\beta' = 1 + 2b/a\lambda^{3/2}. \tag{4}$$

Taking into account that in a real material there is a large number of defects of various shapes, and also that the effective value of the stress-concentration coefficient decreases with deformation because of the orientational strengthening of the overstressed material, it is expedient to write the expression for the dependence of β' on deformation in a more general form:

$$\beta' = 1 + c\lambda^{-n}, \tag{5}$$

which indirectly takes into account both the geometrical influence and the orientational strengthening of the material. In (5), the coefficient c depends on the inhomogeneity of the material, while the exponent n characterizes the degree of influence of deformation on the stress concentration caused by this inhomogeneity.

From (1), (2), and (5) we obtain:

$$\tau = \tau_0 \exp \frac{U_0 - \omega(1 + c\lambda^{-n})\sigma}{kT}. \tag{6}$$

In long-term strength tests, the time to failure τ usually substantially exceeds the time required for the practical completion of the relaxation process and the establishment of elastic equilibrium.

Hence follows the possibility of using a simple linear relation between stress and deformation (6):

$$\sigma = E_\infty \varepsilon = E_\infty(\lambda - 1), \tag{7}$$

with allowance for which we finally obtain:

$$\tau = \tau_0 \exp \frac{U_0 - \omega[1 + c(\sigma/E_\infty + 1)^{-n}]\sigma}{kT}. \tag{8}$$

If the tests are carried out under conditions of prescribed deformation, this same relation is expediently represented in a somewhat different form:

$$\tau = \tau_0 \exp \frac{U_0 - \omega E_\infty(\lambda - 1)(1 + c\lambda^{-n})}{kT}. \tag{9}$$

After taking logarithms and introducing the additional notations $A = 0.43(\ln \tau_0 + U_0/kT)$ and $B = 0.43(\omega E_\infty/kT)$, relation (9) can be represented in the form:

$$\lg \tau = A - B(\lambda - 1)(1 + c\lambda^{-n}). \tag{10}$$

Relation (10), in which the coefficients A, B, C and the exponent n may be regarded as constants independent of deformation, differs from the analogous expression that can be obtained from (1) by the factor $(1+c\lambda^{-n})$. It is easy to see that at sufficiently large values of λ (a highly oriented polymer material), when $\lambda^n \gg c$, this factor tends to unity and relation (10) passes into the equation of S. N. Zhurkov.

It also follows from the above that, when considering the applicability of relation (10) to the description of the long-term strength of highly elastic materials (rubbers), the greatest interest lies in investigation in the region of small deformation values, where the influence of the factor $1 + c\lambda^{-n}$ is most significant.

At relatively small deformations (less than 100%), under ordinary conditions, fracture of rubbers occurs, however, so slowly that the duration-

strength in this region has been studied only under certain specific conditions that in one way or another contribute to accelerating the process. Acceleration of this kind can be achieved by testing specimens with artificially created regions of stress concentration (specimens with a notch); by applying a dynamic vibrational load to a statically stressed specimen; and by testing specimens in

Fig. 1

Figure 1: Fig. 1

air with a somewhat elevated ozone concentration in comparison with the usual concentration (10^{-5}—10^{-4} instead of the usual $\sim 10^{-6}$%).

Fig. 1. Dependence of durability (time to the appearance of visible cracks) on the degree of imposed stretching for rubbers based on different compounds. Tests at a temperature of $\sim 20^{\circ}$.

It should be borne in mind that the effect of ozone is associated primarily with acceleration of the growth of destructive cracks, and in this sense there is a complete analogy between this phenomenon and the action of many surface-active or chemically aggressive substances that accelerate the destruction of a wide variety of materials, including nonpolymeric ones ([7]).

To verify the ideas developed, the results of several series of tests of rubbers in an ozonized-air medium are presented below. An additional justification of the validity of the chosen method may be provided by the results of the detailed study by Yu. S. Zuev ([7]), who showed that ozone accelerates fracture without changing the general character of the relationship between stress and durability.

In the cited work ([7]) it was also shown that the relationship between the durability of rubbers and deformation is nonmonotonic and is characterized by two extrema: a minimum in the deformation range 10—50% and a maximum at deformations exceeding 100%.

The dependences shown in Fig. 1 were obtained at the Institute of the Tire Industry on a special apparatus in which the tested rubber specimens were kept in a state of prescribed stretching in an air medium containing ozone in the amount 0.00013—0.00016%.

It follows from relation (10) that $A = \lg \tau_{\lambda=1}$. On the other hand, the dependence between $\lg \tau$ and λ in the region of large values of λ must be described by the relation:

$$\lg \tau = A - B(\lambda - 1) \qquad (\lambda^n \gg c). \tag{11}$$

Thus, the constant A can be determined from the experimental curve as the ordinate at the point $\lambda = 1$ of the straight line obtained by extrapolating the linear segment (located in the region of sufficiently large values of λ).

It further follows from (11) that the constant B can be determined as the tangent of the angle of inclination of this same straight line.

To determine the constants c and n, and to check the applicability of relation (10), it is expedient to present the latter in the form:

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

$$\frac{A - \lg \tau}{B(\lambda - 1)} - 1 = Z = c\lambda^{-n}. \tag{12}$$

It follows from (12) that if relation (10) is valid, then the dependence of $\lg Z$ on $\lg \lambda$ must be linear; moreover, the constant n can be determined from the slope of the corresponding straight line, while the intercept cut off by this line on the ordinate axis is $\lg c$.

The corresponding straight lines, obtained on the basis of the experimental data of Fig. 1, are presented in Fig. 2, and Table 1 gives the numerical values of the constants A, B, c, and n for all the rubbers investigated.

Table 1

Rubbers	A	B	c	n
Based on NK	3.0	0.68	40.0	8.35
» » SKI	3.0	0.36	39.8	4.55
» » SKB	2.9	0.77	17.8	5.5
» » SKS-30 ARKM	3.3	0.78	31.5	7.0

It is seen from Fig. 2 that the experimental data are approximated by dependence (12) quite satisfactorily.

In Fig. 3, the good agreement between the experimental and calculated data, using as an example rubber made from SKS-30 ARKM, is also illustrated in the coordinates lifetime–deformation.

Fig. 2. Dependence of the function
$Z = (A - \lg \tau)/B(\lambda - 1) - 1$ on the degree of imposed extension for rubbers based on different bases

Fig. 3. Comparison of calculated and experimental data for the dependence of lifetime on tensile deformation for rubber made from SKS-30 ARKM (O_3 $1.5 \cdot 10^{-4}$%). The continuous curve gives the calculated values

Thus, it may be considered that taking into account the dependence of the constant γ on deformation makes it possible to extend S. N. Zhurkov' s fluctuation theory of strength to highly elastic rupture. A complex, nonmonotonic dependence between lifetime and breaking deformation (or stress) can in this case be

well described by equation (10), containing 4 constants, each of which has a fairly clear physical meaning.

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Note: Figure translations are in progress. See original paper for figures.