OF AGING POLYMERS

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In the general case, failure is a multi-stage topochemical reaction activated by the temperature T and the stress σ and coinciding in outline with the reaction of thermal degradation [1, 2]. With constant temperatures and loads, failure is determined by a small number of effective constants of speeds which, on the assumption that the principle of quasisteadiness of the concentration of intermediate products of the reactions is correct, are expressed through the constants of the speeds of the elementary stages. Under these conditions the phenomenological approach is used in engineering practice with sufficient accuracy; this approach is based on the introduction of the concept of damageability [3-9], whose physical meaning is determined by the method of indication [10]. Here, a change of damageability is described by the equation

$$\frac{d\pi}{dt} = F_1(\sigma, T, \pi),\tag{1}$$

where F_1 takes into account the degree to which the process is concluded and the increase of true stress on junctions with increasing damageability. Failure of polymers is a topochemical reaction concentrated at the apex of growing defects and in the bulk of the material when nuclei of destruction [2] originate. During aging (under the effect of thermal, thermovaidative, and photo degradation, mass transfer, etc.) the molecular characteristics in the bulk of the material change, and the constants of the rate of aging are activated by stress [1, 4]. According to the model of failure, the function F_1 is determined by the growth rate of the defects [2] or, in the final analysis, by the kinetics of the reactions at the crack tips, and that means, by the depth ρ at which various physicochemical processes of destruction, structuring, etc. occur: $F_1(\sigma, T, \pi) = F_1(\sigma, T, \rho, \pi)$.

In view of the strong dependence of the constants of the speeds on stress σ and the stress concentration at the tip of the flaw, it may be taken in the first approximation that ρ is independent of σ [5]. In that case we have an explicit dependence of F_1 on time. In bulk failure [1], we have another special case where F_1 is explicitly independent of time.

Since it is difficult to identify several stages of mechanical destruction from standard experiments for determining the time to failure τ_0 with constant values of σ_0 , T_0 , ρ_0 , it is often taken that $F_1(\sigma, T, \rho, \pi) = f_1(\sigma, T, \rho) \cdot f_2(\pi)$ (we will call this process of failure simple). When in this case Eq. (1) is used for predicting endurance with variable σ , T, and $\rho = \rho_0 = \text{const}$, it causes the history of change of σ , T to be ignored. Correct prediction based on revealing the main stages of the process [1] requires a much larger body of experimental data.

Moreover, when this last approach is put into effect it gives rise to fundamental difficulties connected with the incorrectness of the principle of quasisteady conconcentrators with variable stresses [1]. In engineering practice, the history of change of the load is therefore taken into account with the aid of methods adopted in strain and fracture mechanics of solids and using integral operators with convolution-type kernels [6-9]. These criteria do not take the increase of true stress on junctions with increasing damageability into account; they postulate the simplest regularities of change $\pi = \pi(t)$ with constant values of σ , T, ρ , which is not always in agreement with the experiments [11, 12].

We attempted obtaining an integrodifferential criterion of strength which would be free of the above shortcomings.

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We take it that with constant σ , T, ρ , the kinetics of change of π is described by Eq. (1). In the fairly general case with variable σ , T, ρ the accumulation of damage can be represented (in analogy with [9]) by the integral equation

$$\Phi(\pi) = \int_{0}^{t} Q(t - \xi) dp(\sigma, T, \rho, \pi), \qquad (2)$$

where the effect of π on the function $p(\sigma, T, \rho, \pi)$ describes the increase of true stress on the junctions with increasing π ; the function p is discontinuous with a value equal to zero for $\xi=0$. In accordance with the physical sense, $\Phi(\pi)$ and $p(\sigma, T, \rho, \pi)$ are strictly monotonically increasing functions of their arguments. When the load is constant, the solutions of (1) and (2) coincide. To find the functions Φ , p we assume that $Q(t)=t^{\alpha}$.

Let us first examine the case when $\alpha = 1$. Using the integral (2) in parts, we obtain:

$$\Phi(\pi) = \int_{0}^{t} \rho(\sigma, T, \rho, \pi) d\xi.$$
 (3)

Differentiating equality (3) with respect to time, we write:

$$\frac{d\pi}{dt} = \left(\frac{\partial \Phi}{\partial \pi}\right)^{-1} \rho\left(\sigma, T, \rho, \pi\right). \tag{4}$$

By choosing corresponding values of Φ , p (e.g., $\Phi(\pi) = \pi$), we can attain that the solutions of (1), (4) coincide, i.e., for $\alpha = 1$ Eq. (2) contains arbitrary schemata of mechanical destruction described by the dependence (1).

In the case $\alpha \neq 1$ we make the additional assumptions that with σ , T, ρ = const, the process of failure is simple and $p(\sigma, T, \rho, \pi) = p_1(\sigma, T, \rho)p_2(\pi)$.

Without loss of generality it may be assumed that $p_1(+0) = 1$, $p_2(+0) = 1$, $p_1(0) = p_2(0) = 0$. Then, with σ , T, ρ = const, it follows from (1), (2) that

$$tf_{1}(\sigma, T, \rho) = \int_{0}^{\pi} \frac{d\pi}{f_{2}(\pi)} = \tilde{f}(\pi);$$

$$\Phi(\pi) \int_{0}^{t} (tp_{1}^{1/\alpha}(\sigma, T, \rho) - \xi p_{1}^{1/\alpha}(\sigma, T, \rho)^{\alpha} dp_{2}(\pi(\xi)).$$
(5)

With the adopted assumptions the solutions of (1), (2) coincide if and only if $p_1^{1/\alpha}(\sigma, T, \rho) = af_1(\sigma, T, \rho)$ ($\alpha = const$, not depending on σ , τ , τ). Without loss of generality, we take it that $\alpha = 1$. Then

$$\Phi(\pi) = \int_{0}^{\pi} (\tilde{f}(\pi) - \tilde{f}(\xi))^{\alpha} dp_{2}(\xi).$$
 (6)

With the examined constraints on the form of the functions Q, p, criterion (2) encompasses the known integral criteria [3-9]. For instance, with $\Phi(\pi) = \pi$, $p_2(\pi) = 1$ and $\rho(t) = 1$ we obtain Bart's criterion [8]. With the additional assumptions that $\alpha = 1$, p_1 (σ , T, 1) = $\frac{1}{\tau(\sigma, T, 1)}$, from (2) follows Baily's criterion [4], and with $p_1 = \sigma$ and $p_1 = 1/\tau(\sigma)$, Il'yushin's and Moskvitin's criteria [6, 7]. For aging materials with $\rho \neq \text{const}$ we adopt $\Phi(\pi) = \pi$, $p_2(\pi) = 1$. Then with $\alpha = 1$, p_1 (σ , T, ρ) = $\frac{1}{\tau(\sigma, T, \rho)}$ we obtain Baily's generalized criterion for aging bodies, and with p_1 (σ , T, ρ) = $\tau^{\beta}(\sigma, T, \rho)$ the criterion suggested previously [9].

Let us dwell more in detail on the practical utilization of criterion (1), (2). For elastomers we may take as $f_1(\sigma, T, \rho)$ (for $\rho = 1$) Aexp $\left(\frac{U}{RT}\right)\sigma^{\beta}$, for brittle and oriented polymers Aexp $\left(\frac{-U+\gamma\sigma}{RT}\right)$. According to data of [5], for many elastomers to a depth of transformation of 30-50% $\tau = B\rho\sigma^{-m}\exp\left(-\frac{U}{RT}\right)$. Then $f_1(\sigma, T, \rho) = A\frac{1}{\rho}\sigma^{m}\exp\left(\frac{U}{RT}\right)$.

In the general case, to find $f_1(\sigma, T, \rho)$ it is necessary to investigate endurance on specimens preliminarily aged to different depths of transformation [5, 11] or to use the de-

pendences $\pi=\pi(t)$ obtained in physical experiments for σ , T, $\rho=const.$ The kinetic regularities of change of π (the form of the function $f_2(\pi)$) may be determined from the known criteria of strength for σ , T, $\rho=const.$

For instance, in Kachanov's criterion [3] $f_2(\pi) = \pi(1-\pi)^\gamma$, in Baily's criterion [4] $f_2(\pi) = 1$, in Il'yushin's criterion [6] $f_2(\pi) = \pi^{-\beta}$, which qualitatively corresponds to the kinetics of accumulation of damage in oriented polymers [12]. For nonoriented polymers [13] it is apparently possible to take $f_2(\pi) = \nu + (\beta - \pi)\gamma$. When there is experimental information $\pi = \pi(\sigma, T, \rho, t)$ obtained with the aid of physical methods (e.g., electron paramagnetic resonance, small-angle scatter of x-rays, etc.), we need not confine ourselves to specifying a priori the form of the function f_2 . Differentiating the extremal curves $\pi = \pi(\sigma, T, \rho, t)$ by numerical methods, we transform them in coordinates $\hat{\pi} \sim \pi$ (a similar procedure is used in non-isothermal kinetics). Then $f_2(\pi)$ is specified in the form of a table, which is not difficult with a modern computer, and $f_1(\sigma, T, \rho)$ can be found, e.g., by the method of transformation.

Then we determine analytically or numerically the monotonically increasing functions $f(\pi)$ and $p_1(\sigma)$. From the physical prerequisities it follows that with $\alpha>0$, $p_2(\pi)$ increases monotonically. Then $\Phi(\pi)$ from (6) always exists, it is unique and is a monotonically increasing function. We find $\Phi(\pi)$ from (6) according to the known values of $\tilde{f}(\xi)$, $p_2(\xi)$ analytically, which is usually impossible in elementary functions, or else with the aid of the known numerical methods of solving integral equations. In the simplest case $f_2(\pi)=(1-\pi)^{-\beta}$ [1-3], the contribution of damage π to stress concentration on a single defect can also be determined by the methods of the self-consistent field [14]. Since individual parameters of (2) (e.g., α) cannot be found with σ , T, ρ = const, we determine them in dynamic change of σ , T, ρ , as for the criteria suggested in [7-9].

Example. Let $\tau = B\sigma^{-m}$, $\rho = 1$, $f_1(\sigma) = \frac{m+1}{B}\sigma^m$, $f_2(\pi) = (1-\pi)^{-m}$. We postulate that the dependence $p_1(\sigma)$, like in Il'yushin's criterion, is linear. Then

$$p(\sigma, \pi) = \left(\frac{m+1}{B}\right)^{1/m} \frac{\sigma}{1-\pi}; \qquad \alpha = \frac{1}{m};$$

$$\Phi(\pi) = \int_{0}^{\pi} \left(\frac{1}{m+1}\right) \left[(1-\xi)^{m+1} - (1-\pi)^{m+1} \right]^{1/m} d\frac{1}{1-\xi}.$$
(7)

We compare the different criteria of strength on the basis of evaluations of the safety factors η at the instant of failure in the regime of cyclic change of σ , and also in loading and unloading (regimes 1, 2, 3, respectively) [8]. For the random sample η_1, η_2, \ldots the evaluations of the sample mean m_{η} and of the sample dispersion σ_{η}^2 according to Baily's, Il'yushin's, and Moskvitin's criteria and (2), (7) (criteria I, II, III, IV), respectively, are equal to 0.963; 0.953; 0.97; 0.99 and 1.42·10^-2; 0.53·10^-2; 7.84·10^-4; 2.89·10^-4. The parameter of nonlinearity m'=18.8 in criterion III is determined in regime 1. In calculations of m_{η} , σ_{η}^2 the possibilities of prediction of criterion III in regimes 2, 3 were evaluated. It was found that m' does not lie in the range of permissible values $m' \leqslant m-1=13.51$. From a comparison of m_{η} , σ_{η}^2 for different criteria the advantage of criterion IV can be seen.

Thus the integrodifferential criterion of strength of aging materials suggested in the present article generalizes the previously known criteria [3-9]. The criterion takes into account the history of the change of load, temperature, aging processes, and also the increases of the true stress in the material with increasing damageability, and it describes any desired kinetic schema of simple failure for constant σ , T, ρ .

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FAILURE OF ORGANIC GLASS AFTER ALTERNATING LONG-

TERM AND CYCLIC LOADING

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The Palmgren-Meiner hypothesis of accumulation of damage, or the rule of linear summing of damage, was suggested for describing failure under conditions of fatigue [1]. For the case of two-stage loading by stresses σ_1 and σ_2 this hypothesis can be formulated as follows.

First the specimen is loaded by stress σ_1 for N_1 cycles, then it is tested at stress σ_2 for N_2 cycles. At the level of the stress σ_2 the tests are continued up to failure of the specimen. We assume that N_{1R} and N_{2R} are the numbers of cycles under stresses σ_1 and σ_2 , respectively, and then N_1/N_{1R} and N_2/N_{2R} are the proportions of damageability in the process of the first and second loading, respectively. According to the Palmgren-Mainer hypothesis

$$\frac{N_1}{N_{1R}} + \frac{N_2}{N_{2R}} = 1. {1}$$

An analogous hypothesis for static testing (creep) was formulated by Robinson [2]. Within the time t_1 the specimen is tested under stress σ_1 , then the tests are continued at stress σ_2 to failure within time t_2 . If we denote by t_1/t_1R and t_2/t_2R the proportions of damageability in the first and second loading, respectively, then in accordance with Robinson's assumptions

$$\frac{t_1}{t_{1R}} + \frac{t_2}{t_{2R}} = 1,\tag{2}$$

where t_{1R} , t_{2R} are the time to failure under stresses σ_1 and σ_2 , respectively.

When long-term and cyclic stresses alternate, the hypothesis of accumulation of damage is written in the following form:

$$\frac{t}{t_R} + \frac{N}{N_R} = 1,\tag{3}$$

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