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МАТЕМАТИЧЕСКИЕ МЕТОДЫ И ИНФОРМАЦИОННЫЕ СИСТЕМЫ В ХИМИЧЕСКОЙ ТЕХНОЛОГИИ

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RESEARCH ARTICLE

Thermal destruction of polymeric fibers in the theory of temporary dependence of strength

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Abstract

Objectives. *This study mathematically describes the mutual influence of micro- and macrostages of the process of destruction of polymer materials and determines its main parameters and limiting characteristics. In addition, a relationship is established between molecular constants characterizing the structure of a material and those characterizing its macroscopic characteristics of strength. Finally, theoretical representations of the thermokinetics of the process of thermal destruction of polymer fibers from the standpoint of the kinetic thermofluctuation concept are developed, which makes it possible to predict the thermal durability of a sample under thermal loading.*
Methods. *The structural–kinetic thermofluctuation theory was used to describe the initial stages of the fracture process and to derive a generalized formula for the rate of crack growth. The mathematical theory of cracks is used to describe the thermally stressed state of a material in the vicinity of an internal circular crack under mechanical and thermal loadings of the sample.*
Results. *A theoretical formula for the full isotherm of durability in the range of mechanical stresses from safe to critical, as well as a theoretical relationship for the time dependence of the strength of polymer fibers under purely thermal loading in the full range of heat loads from safe to critical and at the stage of nonthermal crack growth, is given. The main parameters and limiting characteristics of durability under thermal loading are also indicated.*

Conclusions. *A generalized structural–kinetic theory of the fracture of polymer fibers under purely thermal action on cracked specimens is presented. The developed theory combines three independent approaches: structural–kinetic (thermofluctuation theory), mechanical, and thermodynamic. The obtained theoretical relations are of practical interest for the development of methods for localization, intensification, and control of the crack growth kinetics.*

Keywords: *polymer fibers, time dependence of strength, thermal loads, durability at thermal dest*

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НАУЧНАЯ СТАТЬЯ

Тепловое разрушение полимерных волокон в теории временной зависимости прочности

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Аннотация

Цели. *Математически описать взаимное влияние микро- и макростадий процесса разрушения полимерных материалов, определить его основные параметры и предельные характеристики, установить связь между молекулярными константами, характеризующими структуру материала с одной стороны и макроскопическими характеристиками прочности с другой. Разработать теоретические представления термокинетики процесса теплового разрушения полимерных волокон с позиций кинетической термофлуктуационной концепции, позволяющей прогнозировать термическую долговечность образца при его тепловом нагружении.*
Методы. *Использована структурно-кинетическая термофлуктуационная теория для описания элементарного акта процесса разрушения и вывода обобщенной формулы скорости роста трещины и математическая теория трещин для описания термонапряженного состояния материала в окрестности внутренней круговой трещины при механическом и тепловом нагружениях образца.*
Результаты. *Приводится теоретическая формула полной изотермы долговечности в интервале механических напряжений от безопасного до критического, а также теоретическое соотношение для временной зависимости прочности полимерных волокон при чисто тепловом нагружении в полном интервале тепловых нагрузок от безопасной до критической и на стадии атермического роста трещины. Указаны основные параметры и предельные характеристики долговечности при тепловом нагружении.*
Выводы. *Представлена обобщенная структурно-кинетическая теория разрушения полимерных волокон при чисто тепловом воздействии на образцы с трещиной. Развитая теория объединяет три самостоятельных подхода: структурно-кинетический (термофлуктуационная теория), механический и термодинамический. Полученные теоретические соотношения представляют практический интерес для разработки способов локализации, интенсификации и управления кинетикой роста трещины.*

Ключевые слова: *полимерные волокна, временная зависимость прочности, тепловые нагрузки, долговечность при тепловом разрушении*

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One of the fundamental characteristics of polymer materials is their strength. Even in cases where other properties of polymers are directly used (e.g., optical, electrical, thermal, and magnetic), the material must have a certain minimum strength. In this regard, theoretical methods for assessing the strength of polymers without lengthy laboratory tests are of great importance. This problem is one of the most urgent challenges in the physics and mechanics of polymer strength, both in practical and scientific terms. Its solution is complicated by the need to consider the effect of various operational factors on the strength of polymers, especially when they act together. An important step in this direction is the construction of appropriate generalized models that allow describing the behavior of materials in a wide range of external influences. However, the general methodology for constructing such models is still far from complete, primarily to models describing the processes of thermal destruction of materials caused by the interaction of intense heat fluxes with solids. The direction of research is the content of the problem of thermal strength, whose relevance has grown especially in recent decades in connection with the creation of powerful energy emitters and their use in technological operations. New technological methods in various industries are based on intensive heating of materials by plasma flows, laser, or electron beams.

A huge number of publications have been accumulated describing these processes in nuclear power engineering, aircraft and rocket engineering, space technology, turbine engineering, and others [1–6]. The intensive development in these areas, as well as in microelectronics and electrical engineering, required the creation of structural especially polymer materials that are characterized by thermal shock resistance and thermal strength [7–11]. The issues of thermal destruction of materials have become especially relevant in connection with the practical requirements of modern technology [12–14].

Many aspects of this problem have been theoretically and experimentally developed [15–17]. At the same time, the issues of thermokinetics of the process of destruction of materials, especially polymer fibers, under purely thermal loading have not yet been sufficiently developed in the theory of thermal destruction from the standpoint of the kinetic theory within the framework of the time dependence of strength [18]. This article is devoted to the construction of this theory for polymer fibers and continues the research begun in [19] and [20]. The proposed theory combines three independent approaches, namely, structural–kinetic, mechanical, and thermodynamic, within the framework of mathematical modeling for the study of such complex phenomena. Of greatest interest are the cases of the steady-state thermal state $T(x, y, z)$ in solids with a crack. Experimental data in [21] indicate that with a steady-state heat flow in a body with a crack, there is a significant increase in temperature stresses caused by a local increase in the value of the temperature gradient in a small vicinity of the crack fluctuation volume.

It can be assumed that thermoelastic expansion fields, like their mechanical analogs, increase the stress intensity at the crack tip, forcing it to grow. Experiments confirm this assumption [22]. A polymer sample in the form of a bar (final solid cylinder) with an internal disk-shaped axisymmetric crack was exposed to a heat flow along the sample symmetry axis orthogonal to the crack. As the sample was heated, the stress state of the sample changed: the stress concentration increased in the (small) circular vicinity of the crack, and after a while, the sample collapsed. Since the mechanical load remained unchanged during the experiment, the factor determining the fracture was the thermoelastic field. Thus, this case is of particular interest for the theory of thermal destruction from the standpoint of the kinetic thermofluctuation concept: it is necessary to describe the growth of the fracture crack and calculate the corresponding durability, main parameters, and limiting characteristics of the thermal destruction process, depending on the type of thermal load, physicomechanical, and thermophysical characteristics of the material and its structure. This is important in order to develop methods of localization, intensification, and control of the kinetics of crack growth. It is obvious that knowledge, prevention, and control of this kind of process is an urgent task of materials science.

The corresponding model concepts are based on experimental data [18, 20] obtained on the basis of direct physical methods on the accumulation of violations in loaded samples (i.e., force perturbation and rupture of bonds in polymers), on submicroscopic cracks and their characteristics, on fractographic studies of rupture surface, on the kinetics of the growth of the main crack when the specimen is stretched with a uniform stress σ = const, and on temperature–time dependence of durability in the full range of stresses $\sigma_0 \le \sigma \le \sigma_{cr}$ from safe to critical.

MAIN APPROACHES IN STUDYING THE STRENGTH OF SOLIDS

To date, studies of the problem of brittle fracture of solids (in particular, polymer materials) are developing in two main directions: mechanical and kinetic approaches. The first direction is associated with calculating the strength of defective bodies by methods of fracture mechanics. It is based on the difference between theoretical and real values of strength, which is interpreted in terms of the classical elastic model of Griffith [23]. The mechanical approach uses the concept of a limiting state as a fracture criterion, upon reaching which fracture occurs. The second direction is associated with the development of the kinetic thermofluctuation concept based on the ideas of Frenkel [24] on thermal motion in solids. In the kinetic approach, main attention is paid to the atomic–molecular process of destruction, and the rupture is considered as the result of the gradual development and accumulation of microdestructions or as the process of development of a microcrack. In this concept, the durability of the body under load is taken as a fundamental quantity that determines the strength and is the basis for the kinetic thermofluctuation theory of fracture, which finds its natural expression in the equations of the time dependence of strength $\tau = (\sigma, T)$ [19]. Both aspects should be included in a complete description of the polymer degradation process in order to construct a generalized theory of strength that considers the structural features of polymer materials. The first results in this direction are presented in an author's survey [21] and in a book [20].

The urgent need for generalized approaches to solve the problem of the strength of solids is now generally recognized. According to the authors [18]: "For further progress in the theory of fracture, it is necessary to develop both physical research and phenomenological, mechanical theories of fracture. The connection between both approaches can be seen primarily in the further development of the concept of damage accumulation at different levels (from the molecular level to the propagation of main cracks). It is necessary to compare the fracture models with the results of direct experiments, where the damage parameters are directly measured."

Temperature–time dependence of strength

A characteristic feature of the durability depending on $\lg\tau\ (\sigma, T)$ at different temperatures is the presence of a linear section described by the Zhurkov equation [18]:

$$\tau = \tau_0 \exp\left(\frac{U_0 - \gamma\sigma}{kT}\right), \tag{1}$$

where τ_0, U_0, and γ are material constants, which can be considered constant in a certain range of stresses and temperatures, corresponding to a certain mechanism of destruction [20, 25]. Equation (1) has certain limits of applicability. The lower limit of its applicability is the safe stress, and the upper (maximum) limit is the critical stress σ_{cr}. Experiments have confirmed the existence of safe and critical voltages. Thus, in the region of small values of σ for the brittle state, where deformation processes in polymers are weakly expressed, a deviation of the dependence $\lg\tau\ (\sigma, T)$ from linear is observed and a sharp rise in the life curve occurs. The curve asymptotically approaches the vertical $\sigma = \sigma_0$:

$$\lim_{\sigma\to\sigma_0} \lg\tau(\sigma, T) = +\infty, \tag{2}$$

corresponding to the safe stress σ_0. In quasi-brittle fracture, the deflection is smoother, which is associated with the relaxation properties of polymers; however, in this case, condition (2) also holds. According to the authors of [26], there is a certain limit for solids, below which, in the absence of aggressive media, destruction does not occur. In the region of high stress intensity ($\sigma \ge \sigma_{cr}$), a transition to the limiting value τ_{cr} is also experimentally observed, associated with the existence of the maximum growth rate of the fracture crack ν_{cr}. Thus, Kerkhoff [27] showed the tendency of the fracture crack velocity in the region of high stresses to the value ν_{cr} = const.

Experiments carried out on glass and rosin [28] showed that ν_{cr} does not depend on temperature and practically on voltage, indicating that it is a nonthermal value. With a sample width of $L = 3$ mm and a value of $\nu_{cr} = 700–800$ m/s characteristic of polymers, the τ_{cr} value is 10^{-6} to 10^{-5} s. The existence of a segment of the curve $\lg\tau_{cr} = \text{const}$ for $\sigma \geq \sigma_{cr}$ was theoretically predicted in [29] and later experimentally confirmed in [30]. On the lgτ (σ, T) graph, this case corresponds to the bend of the curve toward constant values of durability, which is associated with the transition to the nonthermal mechanism of destruction. Analyzing the state of the matter, the author of [20] comes to the following conclusion: the dependence lgτ (σ, T) has the form shown in Fig. 1. In the range of stresses (σ_0, σ_{cr}), not too close to the safe and critical, the dependence lgτ (σ, T) is linear. In the vicinity of σ_0 and σ_{cr}, the indicated curve bends to the vertical and horizontal asymptotes, respectively, based on the fulfillment of the limit relation (2), as well as on the following condition:

$$\lim_{\sigma\to\sigma_{cr}} \tau(\sigma,T) = \tau_{cr}\,. \qquad (3)$$

Shown in Fig. 1 is the graphical dependence lgτ (σ, T) in the full range of stresses [σ_0, σ_{cr}], which is called the complete isotherm of durability. The graph shows four areas of manifestation of the thermofluctuation mechanism of destruction: I ($\sigma \leq \sigma_0$) and IV ($\sigma \geq \sigma_{cr}$) are the boundary areas of the safe and nonthermal mechanisms, II ($\sigma_0 < \sigma < \sigma_{cr}$) is the area of pure thermal fluctuation mechanism, and III ($\sigma_f < \sigma < \sigma_{cr}$) is the transition region, where the nonthermal mechanism begins to appear.

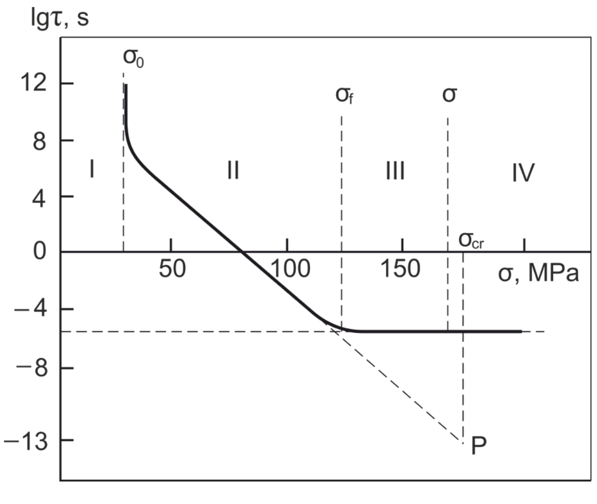

Fig. 1. Temperature–time dependence of strength in the full stress range.

Ideological research scheme

Registration of submicroscopic cracks in real polymer fibers made it possible to establish their disk-like shape, their location within the sample volume perpendicular to the loading axis, and very small sizes of microcracks (900–3000 Å) with a $2R^\bullet$ sample diameter of several millimeters. It was also established that the critical crack length R_{cr} is independent of the sample cross-section. Thus, for the characteristics of the crack, there is a very important relation:

$$\lambda \ll R_0 \leq R(t) \leq R_{cr} \leq R^\bullet, 0 \leq t \leq \tau\,, \qquad (4)$$

where R_0 is the initial radius of the crack, $R(t)$ is the current value of the radius, τ is the sample lifetime, and λ is the fluctuation propagation of the crack. A direct study of the kinetics of the fracture process in each specific case of loading a polymer sample (e.g., thermal, mechanical, and electrical) is carried out on the basis of the analytical formula for the rate of crack growth as a function of its current radius $R(t)$, stress field $\sigma^\bullet$ in the defect region V_a (fluctuation volume), temperature T in the circular vicinity of the crack, and molecular constants characterizing the polymer structure, as well as the elementary act of breaking strained bonds:

$$v = v(R,\sigma^\bullet,T_в,V_а,U,...), \qquad (5)$$

where U is the activation energy of the bond-breaking process in the fluctuation volume. The main problem in this case is to obtain a specific expression for (5), taking into account the basic physical laws of the kinetics of the destruction process, which were experimentally revealed for this case, and their influence on the elementary act of destruction in the volume V_a. Local stress in (5) $\sigma^\bullet = \varphi(\sigma, \beta, R\ldots)$ is one of the most important strength characteristics. The value of $\sigma^\bullet$ depends on the external stress σ applied to the sample, current radius of the crack $R = R(t)$, geometry of the sample, configuration of the crack and its location in the sample, and stress concentration factor β. The value $\sigma^\bullet$ is calculated by the methods of brittle fracture mechanics based on the solution of boundary value problems of the mathematical theory of cracks. In fact, on the basis of (5), the mutual influence of the macro- and microstages of the fracture process is studied. Using (5), the main parameters and limiting characteristics of the fracture process are determined, a connection is established between the molecular constants characterizing the structure of materials and the macroscopic characteristics of strength, and finally a methodology for calculating the durability of a specimen under various test conditions is being developed. Thus, within the framework of this research scheme, three approaches are combined: structural–kinetic approach (thermal fluctuation theory for describing the initial stages of the of the destruction process, which is associated with the derivation of (5)), mechanical approach (methods of brittle fracture mechanics for describing local stress at the crack tip under conditions of a certain specimen loading mode), and thermodynamic approach (to calculate the value of the safe voltage).

The durability of the specimen $\tau = \tau(\sigma, T)$ (T is the test temperature, which is generally different from the temperature T_t at the crack tip) is the sum of the times of the rupture process at the first (fluctuation) stage $\tau_f(\sigma, T)$ when the crack grows at a rate (5) from the initial radius R_0 to the critical radius R_{cr} and the second (nonthermal) stage σ_{cr} with the limiting velocity of fracture propagation in a solid $v_{cr} = 0.38\sqrt{E/\rho}$ (Roberts–Wells formula), where E is Young's modulus and ρ is the material density:

$$\tau = \tau_f + \tau_{cr} = \int\limits_{R_0}^{R_{cr}} \frac{dr}{v(r, \sigma^{\bullet}, T_t, \ldots)} + \frac{R - R_{cr}}{v_{cr}}. \tag{6}$$

STRESS INTENSITY COEFFICIENTS IN THE REGION OF A CIRCULAR CRACK

Calculation of the magnitude of the local stress $\sigma^{\bullet}$ is fundamental in the development of this theory of fracture. Based on (4), a fiber-like sample is interpreted as an elastic space (x, y, z) with an internal circular axisymmetric crack $0 \le r \le R(r^2 = x^2 + y^2)$ in the plane $z = 0$. Considering that the fracture of brittle polymers is localized in a small vicinity of a crack in the volume (V_a), for the mathematical theory of cracks, it is of interest to study the asymptotic distribution of stresses near the crack front in a homogeneous, elastic, and isotropic continuum. The problem is to find the stress intensity factors $K^{(M)}$ of mechanical and $K^{(T)}$ thermal loads in the asymptotic representation of axial (breaking bond) stress $\sigma_{zz}(r,0) = K(\sigma, R)/\sqrt{2(r-R)}, r > R$ from the basic equations of thermomechanics. It should be noted that the approach proposed below for finding the asymptotic solution of the problem is of independent interest for the mathematical theory of cracks.

In a cylindrical coordinate system (r, φ, z) under the conditions of symmetry about the z axis, as well as symmetry about the plane $z = 0$, the formulated problem is reduced to solving a thermoelastic axisymmetric problem for a half-space $z \ge 0$, consisting of the equilibrium (7), geometrical (8), and physical (9) equations:

$$\left.\begin{aligned} &\frac{\partial \sigma_{rr}}{\partial r} + \frac{\partial \sigma_{rz}}{\partial z} + \frac{\sigma_{rr} - \sigma_{\varphi\varphi}}{r} = 0 \\ &\frac{\partial \sigma_{rz}}{\partial r} + \frac{\partial \sigma_{zz}}{\partial z} + \frac{\sigma_{rz}}{r} = 0 \end{aligned}\right\} ,\ z > 0,\ r > 0 \tag{7}$$

$$\left.\begin{aligned} &\varepsilon_{rr} = \frac{\partial U}{\partial r}; \varepsilon_{\varphi\varphi} = \frac{U}{r}; \varepsilon_{zz} = \frac{\partial W}{\partial z} \\ &\varepsilon_{rz} = \frac{1}{2}\left(\frac{\partial U}{\partial z} + \frac{\partial W}{\partial r}\right) \end{aligned}\right\} \tag{8}$$

$$\left.\begin{aligned} &\sigma_{rr} = 2G\left[\varepsilon_{rr} + \frac{v}{(1-2v)}e - \frac{1+v}{(1-2v)}\alpha_T T\right] \\ &\sigma_{\varphi\varphi} = 2G\left[\varepsilon_{\varphi\varphi} + \frac{v}{(1-2v)}e - \frac{1+v}{(1-2v)}\alpha_T T\right] \\ &\sigma_{zz} = 2G\left[\varepsilon_{zz} + \frac{v}{(1-2v)}e - \frac{1+v}{(1-2v)}\alpha_T T\right] \\ &\sigma_{rz} = 2G\varepsilon_{rz}. \end{aligned}\right\} \tag{9}$$

Here, $\sigma_{ij} = \sigma_{ij}(r, z)$, $\sigma_{ij} = \sigma_{ij}(r, z)$ are the components of the stress tensor and strain tensor ($i, j = r, \varphi, z$), respectively; $U = U(r, z)$ and $W = W(r, z)$ are the components of the displacement vector in the radial and axial directions; $T = T(r, z)$ is the temperature function, ν is Poisson's ratio, G is the shear modulus, α_T is the coefficient of linear thermal expansion, and e is the volumetric deformation:

$$e(r, z) = \frac{\partial U}{\partial r} + \frac{U}{r} + \frac{\partial W}{\partial z}. \tag{10}$$

The boundary conditions for the problem posed are as follows:

$$\sigma_{zz}(r, z)\big|_{z=0} = -\sigma, \tag{11}$$

$$\sigma_{rz}(r, z)\big|_{z=0} = 0,\ r \ge 0, \tag{12}$$

$$W(r, z)\big|_{z=0} = 0,\ r > R, \tag{13}$$

$$\left|\sigma_{ij}(r, z), W(r, z), U(r, z), \varepsilon_{ij}(r, z)\right| < \infty,\ r \ge 0,\ z \ge 0. \tag{14}$$

The temperature function included in (5) is a solution to the heat problem:

$$\frac{\partial^2 T}{\partial r^2}+\frac{1}{r}\frac{\partial T}{\partial r}+\frac{\partial^2 T}{\partial z^2}=0,\ z>0,\ r>0, \qquad (15)$$

$$\frac{\partial T(r,z)}{\partial z}\Big|_{z=0}=\frac{1}{\lambda_{\mathrm{T}}}q_{\mathrm{T}},\ \ 0\le r<R, \qquad (16)$$

$$T(r,z)\big|_{z=0}=0,\ \ r>R, \qquad (17)$$

$$\frac{\partial T(r,z)}{\partial z}\Big|_{z=\infty}=0,\ \ r>0, \qquad (18)$$

where λ_{T} is the thermal conductivity of the material and q_{T} is the value of the heat flux entering the sample through a unit of area per unit of time. In (15)–(18), for the convenience of the solution, which does not affect the final result, the heat problem is written with respect to the reduced function $T(r, z) = T(r, z)^* + (q_{\mathrm{T}} / \lambda_{\mathrm{T}})z$, where $T^*(r, z)$ is the temperature function, corresponding to the initial experiment when the heat flow enters the sample through its end $(\partial T^* / \partial z)\big|_{z=+\infty} = -(q_{\mathrm{T}} / \lambda_{\mathrm{T}})$. Furthermore, it is assumed that the flow does not go $(\partial T^* / \partial z\big|_{z=0}=0,\ 0\le r<R)$, and the transfer of heat by radiation through the crack can be neglected, which is true for not too high temperatures.

A similar problem in the presence of only mechanical loads and only surface temperature of the crack was studied by Sneddon and by Sheil, respectively. Borodachev considered both cases in the original setting, generalizing at the same time the dependences reported by Goodyear and Florence as well as those of Sneddon and Lovengrub [20, 31, 32]. Below is a different approach to solve the problem that is more rational from the point of view of the generality of the results obtained.

Let us introduce the thermoelastic potential of displacements $\Phi(r, z)$ by the following relations [33]:

$$U=\frac{\partial\Phi}{\partial r};W=\frac{\partial\Phi}{\partial z}\qquad (e(r,z)=\Delta\Phi(r,z)). \qquad (19)$$

If we substitute (9) in (7) and then (8) into the obtained relation, then equalities (7)–(9) can be written in displacements:

$$\left.\begin{aligned}&\Delta U-\frac{1}{r^2}U+\frac{1}{1-2\nu}\frac{\partial e}{\partial r}-\frac{2(1+\nu)}{1-2\nu}\alpha_{\mathrm{T}}\frac{\partial T}{\partial r}=0\\&\Delta W+\frac{1}{1-2\nu}\frac{\partial e}{\partial z}-\frac{2(1+\nu)}{1-2\nu}\alpha_{\mathrm{T}}\frac{\partial T}{\partial z}=0\end{aligned}\right\} \qquad (20)$$

Substituting relation (19) into (20) and integrating the first of them over r and the second over z, we find the following equation:

$$\Delta\Phi(r,z)=\frac{(1+\nu)\alpha_{\mathrm{T}}}{1-\nu}T(r,z). \qquad (21)$$

If any particular solution of (21) is found, then strains and stresses can be calculated based on this solution as follows:

$$\bar{\varepsilon}_{rr}=\frac{\partial^2\Phi}{\partial r^2};\bar{\varepsilon}_{\varphi\varphi}=\frac{1}{r}\frac{\partial\Phi}{\partial r};\bar{\varepsilon}_{zz}\frac{\partial^2\Phi}{\partial z^2};\bar{\varepsilon}_{rz}=\frac{\partial^2\Phi}{\partial r\partial z}; \qquad (22)$$

$$\left.\begin{aligned}&\bar{\sigma}_{rr}=2G\left(\frac{\partial^2\Phi}{\partial r^2}-\Delta\Phi\right);\bar{\sigma}_{\varphi\varphi}=2G\left(\frac{1}{r}\frac{\partial\Phi}{\partial r}-\Delta\Phi\right)\\&\bar{\sigma}_{zz}=2G\left(\frac{\partial^2\Phi}{\partial z^2}-\Delta\Phi\right);\bar{\sigma}_{rz}=2G\frac{\partial^2\Phi}{\partial r\partial z}\end{aligned}\right\} \qquad (23)$$

In the Hankel expression

$$\bar{\Phi}(\xi,z)=\int_0^\infty rJ_0(\xi r)\Phi(r,z)dr,$$

$$\bar{T}(\xi,z)=\int_0^\infty rJ_0(\xi r)T(r,z)dr \qquad (24)$$

the general solutions of (15) and (21) have the following forms, respectively:

$$\bar{T}(\xi,z)=\bar{T}(\xi,0)\exp(-\xi z), \qquad (25)$$

$$\bar{\Phi}(\xi,z)=$$
$$=\left[\frac{1}{2G\xi^2}\bar{\sigma}_{zz}(\xi,0)-\frac{z}{2\xi}\frac{(1+\nu)}{(1-\nu)}\alpha_{\mathrm{T}}\bar{T}(\xi,0)\right]\exp(-\xi z). \qquad (26)$$

The unknown functions of ξ entering into (26) are found from boundary conditions (11) and (13) and from relations (19) for $\bar{W}(\xi,z)=d\bar{T}(\xi,z)/dz$. This leads to a dual integral equation

$$\left.\begin{aligned}&\int_0^\infty \xi\bar{f}(\xi)J_0(\xi r)d\xi=h(r),\ \ 0\le r<R,\\&\int_0^\infty \bar{f}(\xi)J_0(\xi r)d\xi=0,\ \ r>R\end{aligned}\right\} \qquad (27)$$

where the following labels are made:

$$\left.\begin{aligned}\bar f(\xi) &= \frac{1-\nu}{G}\bar\sigma_{zz}(\xi,0)+(1+\nu)\alpha_{\text{T}}\bar T(\xi,0)\\ h(r) &= -\frac{1-\nu}{G}\sigma+(1+\nu)\alpha_{\text{T}}T_0(r),\ 0\le r<R\end{aligned}\right\} \tag{28}$$

here, $T_0(r) = T(r, 0)$. The author of this article has previously developed extensive tables of dual integral equations and paired summation series [34]. We find from the tables the solution of the dual integral (27):

$$\bar f(\xi)=\frac{2}{\pi}\int_0^R \sin\eta\xi d\eta\int_0^\eta\frac{yh(y)dy}{\sqrt{\eta^2-y^2}}, \tag{29}$$

where from (28), we find in the space of originals

$$\begin{aligned}&\bar\sigma_{zz}(r,0)=\\ &=-\frac{2G}{\pi(1-\nu)}\int_0^R\frac{\eta d\eta}{(r^2-\eta^2)^{3/2}}\int_0^\eta\frac{yh(y)dy}{\sqrt{\eta^2-y^2}}-\frac{(1+\nu)\alpha_{\text{T}}G}{(1-\nu)}T(r,0).\end{aligned} \tag{30}$$

Relation (30) refers to the case when either the temperature (then at $r > R$, the value is $\partial T/\partial z\big|_{z=0}=0$), or heat flow is set.

According to Irwin [18], the asymptotic behavior of the voltage $\bar\sigma_{zz}$ in the region of the circular crack is expressed as

$$\left[\bar\sigma_{zz}(r,0)\right]_{\max}=\frac{K(\sigma,R)}{\sqrt{2(r-R)}},\ r>R, \tag{31}$$

where $K(\sigma, R)$ is the stress intensity factor, i.e., parameter reflecting the redistribution of stresses in the body due to the presence of a crack:

$$K(\sigma,R)=\lim_{r\to R+0}\sqrt{2(r-R)}\left[\bar\sigma_{zz}(r,0)\right]. \tag{32}$$

In (30), we sequentially consider the cases of only mechanical loading at a constant test temperature ($T_0(r) = 0$) and only thermal loading in the absence of mechanical stress. From (32) in the first case, we have $K^{(\text{M})}=(2/\pi)\sigma\sqrt{R}$, and from relation (31), the maximum tensile stress in the vicinity of a circular crack, attained in the plane of the crack, is expressed as follows:

$$\left[\bar\sigma_{zz}^{(\text{M})}(r,0)\right]_{\max}=\frac{\sigma\sqrt{2R}}{\pi\sqrt{r-R}}. \tag{33}$$

Direct experiments by IR spectroscopy to measure stresses on individual chemical bonds for solid polymers [18] showed that as the crack front approaches the maximum stress bonds, the load increases up to a certain value, after which it remains constant and exceeds the average stress on bonds in sample volume by several orders of magnitude. Such bonds are highly deformed and break in the first place. Their rupture is due to the stress applied to the bond, which is spaced from the crack tip at the distance of its fluctuation advance. Thus, the sought local stress in the vicinity of a circular crack can be written as $\sigma^*_{(\text{M})}=(\sqrt{2}/\pi)\sigma\sqrt{R/\lambda}$, but in the final form, it is expressed as follows:

$$\sigma^*_{(\text{M})}=\sigma\beta(R_0)\sqrt{R/R_0}, \tag{34}$$

where $R = R(t)$ is the variable radius of the growing crack, $2R_0$ is the diameter of the initial (in the sample) circular microcrack, and $\beta(R_0)$ is the stress concentration factor for an internal circular crack defined as

$$\beta(R_0)=0.5\sqrt{R_0/\lambda}. \tag{35}$$

In experiments on creep (σ = const) [18], it was shown that the coefficient β practically does not change during the lifetime of the sample and is determined only by the initial dimensions of the defect in the sample. From (35), we find an estimate of the diameter of the initial microcrack in polymer fibers:

$$R_0=4\lambda\beta^2. \tag{36}$$

According to [18], for oriented fibers (e.g., polyethylene, polypropylene, and polycaproamide) λ = 4 Å, β = 4–7, the value from (36) is the radius of the initial microcrack $\text{R}_0 = (10^{-8}–10^{-7})$ m, which is experimentally confirmed.

Let us further find the local stress with only thermal loading in the modes (15)–(18), for which it is necessary to find the value $T(r, 0)$. In the Hankel expression (24), the solution of (15) with boundary conditions (16)–(18) is reduced to a dual integral equation:

$$\left.\begin{aligned}&\int_0^\infty\xi^2J_0(\xi r)\bar T(\xi,0)d\xi=-(\lambda_{\text{T}}/q_{\text{T}}),\ 0\le r<R\\ &\int_0^\infty\xi J_0(\xi r)\bar T(\xi,0)d\xi=0,\ r>R\end{aligned}\right\} \tag{37}$$

where, according to the tables in [34], we find the equation $\xi\overline{T}(\xi,0) = -(2q_{\mathrm{T}}/\pi\lambda_{\mathrm{T}})\int_0^R \eta \sin\eta\xi d\eta$, as well as the original

$$T(r,0) = -(2q_{\mathrm{T}}/\pi\lambda_{\mathrm{T}})\sqrt{R^2-y^2},\ 0 \le r < R. \tag{38}$$

As a result, from (30)

$$\left[\overline{\sigma}_{zz}^{(\mathrm{T})}(r,0)\right]_{\max} = A\left[\frac{H(R)}{\sqrt{r^2-R^2}} - \int_0^R \frac{H'(\eta)d\eta}{\sqrt{r^2-\eta^2}}\right],\ r > R, \tag{39}$$

$$H(\eta) = \int_0^\eta \frac{y\sqrt{R^2-y^2}}{\sqrt{\eta^2-y^2}}dy,\ \ A = \frac{2E\alpha_{\mathrm{T}}q_{\mathrm{T}}}{\pi^2(1-v)\lambda_{\mathrm{T}}}. \tag{40}$$

From (32) and (39)–(40), we find $K^{(\mathrm{T})} = (A/2)R^{3/2}$ and, at the same time, the desired local stress in the vicinity of a circular crack under thermal loading of the sample in the framework of the thermal problems (15)–(18):

$$\sigma^*_{(\mathrm{T})} = \sigma_{\mathrm{T}}\beta(R_0)(R/R_0)^{3/2}, \tag{41}$$

$$\sigma_{\mathrm{T}} = \frac{0.3\alpha_{\mathrm{T}}q_{\mathrm{T}}ER_0}{(1-v)\lambda_{\mathrm{T}}}\ ;\ \beta(R_0) = 0.5\sqrt{R_0/\lambda}. \tag{42}$$

The resulting ratio for σ_{T} in (42) is a fundamental result for the theory of thermal destruction of polymer fibers: σ_{T} is a mechanical analog of thermal loading and connects the thermophysical, elastic, and structural characteristics of polymers, which makes it possible to trace the influence of each factor on the thermal reaction of a polymer material from the initial circular microcrack. As the temperature T_{t} included in (5), we take the average integral temperature in the ring $R \le r < R + \lambda$ with a fluctuation increase in the radius of the circular crack by λ. This gives the following estimate for the value of T_{t}:

$$T_{\mathrm{t}} = \frac{2q_{\mathrm{T}}\lambda\beta(R_0)}{\lambda_{\mathrm{T}}}. \tag{43}$$

Here, as well as in (42), the relationship between the macro- and microparameters and their influence on the thermal state of the polymer material in the vicinity of the circular crack is traced.

Thus, all quantities included in (5) and (6) have been calculated, which makes it possible to describe the thermokinetics of the growth of a circular crack in polymer fibers and calculate the corresponding durability, both under mechanical and thermal loads.

To complete the solution of the thermoelastic problems (7)–(18), it is necessary to return to boundary condition (12). Since the stresses $\sigma_{rz}(r, z)$ determined in (23) using the thermoelastic potential may not satisfy condition (12), then solution of (20) should be imposed on the resulting solution at $T = 0$ so that condition (12) is satisfied. To do this, we use the Love movement function $L(r, z)$ as follows [1]:

$$\overline{\overline{U}} = -\frac{1}{(1-2v)}\frac{\partial^2 L}{\partial r\partial z};\overline{\overline{W}} = \\ = \frac{1}{(1-2v)}\left[2(1-v)\Delta L - \frac{\partial^2 L}{\partial z^2}\right];\overline{\overline{e}} = \Delta L_z,(L_z = \partial L/\partial z) \tag{44}$$

$$\left.\begin{aligned}
\overline{\overline{\sigma}}_{rr} &= \frac{2G}{(1-2v)}\frac{\partial}{\partial z}\left(v\Delta L - \frac{\partial^2 L}{\partial r^2}\right)\\
\overline{\overline{\sigma}}_{\varphi\varphi} &= \frac{2G}{(1-2v)}\frac{\partial}{\partial z}\left(v\Delta L - \frac{1}{r}\frac{\partial L}{\partial r}\right)\\
\overline{\overline{\sigma}}_{zz} &= \frac{2G}{(1-2v)}\frac{\partial}{\partial z}\left((2-v)\Delta L - \frac{\partial^2 L}{\partial z^2}\right)\\
\overline{\overline{\sigma}}_{rz} &= \frac{2G}{(1-2v)}\frac{\partial}{\partial r}\left((1-v)\Delta L - \frac{\partial^2 L}{\partial z^2}\right)
\end{aligned}\right\} \tag{45}$$

Moreover, the function $L(r, z)$ is in accordance with the biharmonic equation as follows:

$$\Delta^2 L(r,z) = 0,\ r > 0,\ z > 0. \tag{46}$$

If the function $L(r, z)$ is defined, then the total stresses amount to the following equation:

$$\sigma_{ij}(r,z) = \overline{\sigma}_{ij}(r,z) + \overline{\overline{\sigma}}(r,z),\ (i,j = r,\varphi,z). \tag{47}$$

In this case, the movements are always unambiguous. Using the above relations, let us calculate $\sigma_{rz}(r, 0)$:

$$\overline{\sigma}_{rz}(r,0) = \int_0^\infty \left[\frac{2G\xi}{\pi(1-v)}\int_0^R \varphi(\eta)\sin\eta\xi d\eta\right]J_1(r\xi)d\xi, \tag{48}$$

where

$$\left.\begin{aligned}
\varphi(\eta) &= \int_0^\eta \frac{yh(y)dy}{\sqrt{\eta^2-y^2}},\\
h(r) &= -\frac{(1-v)}{G}\sigma + (1+v)\alpha_{\mathrm{T}}T(r,0).
\end{aligned}\right\} \tag{49}$$

If the following condition is required

$$\bar{\bar{\sigma}}_{rz}(r,z)\Big|_{z=0} = -\bar{\sigma}_{rz}(r,0),\ r \ge 0, \tag{50}$$

$$\bar{\bar{\sigma}}_{zz}(r,z)\Big|_{z=0} = 0,\ r \ge 0, \tag{51}$$

then all boundary conditions (11)–(14) will be satisfied.

In the Hankel expression, the bounded solution to (44) has the following form:

$$\bar{L}(\xi,z) = \left[\bar{A}(\xi) + \bar{B}(\xi)z\right]\exp(-\xi z). \tag{52}$$

To determine the constants in (52) from boundary conditions (50)–(51), we write the following equations using (45) and (52):

$$\bar{\bar{\sigma}}_{rz}(r,z) = \\ = \frac{2G}{(1-2\nu)}\int_0^\infty \xi^2 J_1(r\xi)\left[\nu\frac{d^2\bar{L}(\xi,z)}{dz^2} + (1-\nu)\xi^2\bar{L}(\xi,z)\right]d\xi; \tag{53}$$

$$\bar{\bar{\sigma}}_{zz}(r,z) = \\ = \frac{2G}{(1-2\nu)}\int_0^\infty \xi J_0(r\xi)\left[(1-\nu)\frac{d^3\bar{L}(\xi,z)}{dz^3} - (2-\nu)\frac{d\bar{L}(\xi,z)}{dz}\right]d\xi. \tag{54}$$

Equations (51), (52), and (54) give

$$\bar{A}(\xi) = -\frac{(1-2\nu)}{\xi}\bar{B}(\xi). \tag{55}$$

Equations (49), (50), (52), and (53) give:

$$\bar{B}(\xi) = \frac{(1-2\nu)}{\pi(1-\nu)\xi^2}\int_0^R \varphi(\eta)\sin\eta\xi\, d\eta, \tag{56}$$

which concludes in finding the desired solution for (7)–(18).

MAIN PARAMETERS, LIMITING CHARACTERISTICS AND DURABILITY UNDER THERMAL STRESS

Thermofluctuation processes of destruction at the atomic–molecular level are described using the model of weakly coupled harmonic oscillators, where the elementary act of destruction is interpreted as a classical transition through a potential barrier. At the atomic–molecular model, taking into account the frequencies of rupture and restoration of chemical bonds at the crack tip, the average rate of crack growth is described by the following expression [1]:

$$v(l,\sigma^*,T_\text{t}...) = 2\lambda\nu_0\exp\left[-\frac{U - V_a\sigma_0^*}{kT_\text{t}(l,t)}(\sigma^* - \sigma_0^*)\right], \tag{57}$$

where λ is the fluctuation crack propagation upon breaking one or a group of bonds; ν_0 is the frequency of thermal vibrations of the kinetic units involved in breaking and restoring bonds ($\nu_0 \sim 10^{-13}$ s^{-1}); k is Boltzmann's constant; $U = U_0 - qT_\text{t}$ is the activation energy of the destruction process, which linearly decreases with increasing temperature; U_0 is the fracture activation energy extrapolated to absolute zero; q is the coefficient of temperature dependence of activation energy (for polymer (organic) glasses $q \sim 15$–20 J/(mol·K); and σ_0 is the thermal fluctuation fracture threshold (safe overvoltage at the crack tip). For stresses σ that are not too close to and do not exceed the safe critical intensities ($\sigma_0 < \sigma < \sigma_\text{cr}$), respectively, the probability of bond recovery at the crack tip is negligible compared to the probability of their breaking. If we neglect the bond recombination process in the vicinity of the crack tip, the rate of its growth will take on a simpler form:

$$v(l,\sigma^*,T_\text{t}) = \lambda\nu_0\exp\left[-\frac{U - V_\text{a}\sigma_0^*}{kT_\text{t}(l,t)}\right]. \tag{58}$$

In our case, we have

$$v(R,\sigma^*_{(\text{T})},T_\text{t}) = \lambda\nu_0\exp\left(-\frac{U - V_\text{a}\sigma^*_{(\text{T})}}{kT_\text{t}}\right), \tag{59}$$

where all basic values are calculated. Calculating integral (6), we obtain the desired expression for the durability $\tau = \tau_\text{f} + \tau_\text{cr}$ under purely thermal loading of a specimen with an internal circular crack within the thermal models (15)–(18):

$$\tau = \frac{2R_0\exp(-q/k)}{3\lambda\nu_0\alpha\sigma_\text{T}}\exp\left(\frac{U_0 - V_\text{a}\beta\sigma_\text{T}}{kT_\text{t}}\right) + \\ + 2.63R^*\sqrt{\rho/E}\,(1 - 4\lambda\beta^2/R^*), \tag{60}$$

where $\alpha = V_\text{a}\beta / kT_\text{t}$. Several important parameters and limiting characteristics of the fracture process should also be added to these ratios. The characteristic of σ_0 corresponds to the voltage at which a sharp rise in the life isotherm curve is experimentally observed to the region of arbitrarily long-time values. In the kinetic theory, this quantity is introduced by the following relation:

$$\sigma_0 = \alpha_s/(\beta\lambda_m), \tag{61}$$

where α_s is the free surface energy of material (in a vacuum) and λ_m is the pre-breaking bond lengthening. The value from (61) is the safe voltage. It should be emphasized that the question of the existence of a safe stress has been controversial for many decades. Only recently when investigating the true meaning of the Griffith energy criterion for brittle polymers, this article has shown [35] that the value σ_0 coincides with the Griffith (safe) fracture threshold for a disk-shaped crack:

$$\sigma_0 = \sigma_G = \sqrt{\frac{2E\alpha_s}{2R_0(1-\nu^2)}}. \tag{62}$$

Critical stress is expressed as follows:

$$\sigma_{cr} = \frac{U_0 - qT}{V_a\beta}. \tag{63}$$

The main external factor causing the growth of a crack at a rate (59) is the heat load with power q_T, which is one of the stress components in (42). Relationships (61) and (62) (at $T = T_t$) determine the range of stresses from safe $\sigma_T^{(0)}$ to critical $\sigma_T^{(cr)}$, which makes it possible to identify the corresponding values of external thermal stress from safe (64) to critical (65):

$$q_T^{(0)} = \frac{36.3\lambda_T}{\alpha_T}\sqrt{\frac{(1-\nu)\alpha_s}{(1+\nu)E}}R_0^{-3/2}; \tag{64}$$

$$q_T^{(cr)} = \frac{12(1-\nu)\lambda_T\sqrt{\lambda}(U_0 - qT)}{\alpha_T E V_a}R_0^{-3/2}. \tag{65}$$

Thus, the reduced interval of external thermal loading $(q_T^{(0)}, q_T^{(cr)})$ determines the time dependence of strength (60). For values $q_T \geq q_T^{(cr)} (\sigma_T \geq \sigma_T^{(cr)})$ the time dependence (60) ceases to be fulfilled, and the crack grows with a maximum speed ν_{cr}. The latter means that the dependence ($\lg\tau$, σ_T) or ($\lg\tau$, q_T) is parallel to the stress axis σ_T or the heat load axis q_T.

Figure 2 shows the curve of durability for a sample in the form of a monofilament made of organic glass, which was calculated from the following obtained ratios: $\alpha_s = 39 \cdot 10^{-3}$ J/m², $\alpha_T = 8 \cdot 10^5$ grad^{-1}, $\lambda_T = 0.197$ W/(m·K), $\nu_0 = 10^{-13}$ s^{-1}, $\lambda = 12 \cdot 10^{-4}$ μm, $q_T^{(0)} = 210$ W/mm², $q_T^{(cr)} = 1700$ W/mm², $R_0 = 10^{-7}$ m, $U_0 = 133$ kJ/mol, $\beta = 9$, $q = 8.2$ J/(mol·K), $V_a = 1.4 \cdot 10^{-28}$ m³, $R^* = 10^{-3}$ m, $\nu_{cr} = 800$ m/s, $E = 3.93 \cdot 10^9$ N/m², $\rho = 1.2 \cdot 10^3$ kg/m³, $\sigma_0 = 21$ MPa, and $\sigma_{cr} = 168$ MPa.

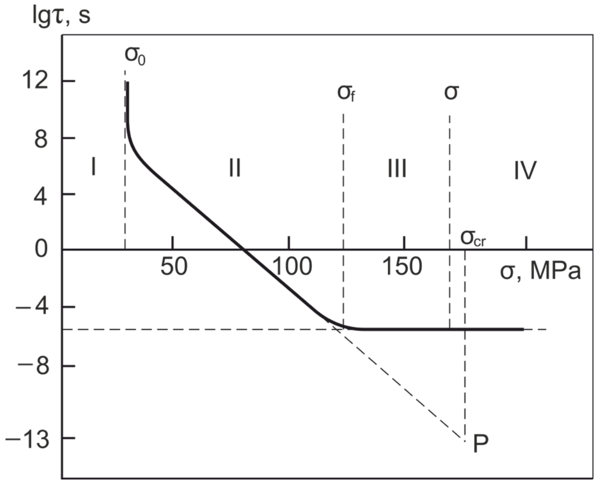

Fig. 2. Life curve for the plexiglass monofilament sample.

The resulting curve gives a clear idea of the possibility of predicting the time dependence of the "thermal" durability of a sample under its thermal loading within the framework of the above thermal model. The calculated relations of dependence (60) contain a complex of physicomechanical, thermophysical, and structural characteristics of a material with a crack, which makes it possible to evaluate their individual influence on the thermokinetics of crack growth and possible control of the process of thermal destruction. Similarly, one can consider other cases of thermal loading of a polymer sample with an internal circular crack, as well as more general ones, when thermal fields are simultaneously coupled with fields of different physical nature, including relaxation processes at the initial stages of heat propagation [36].

CONCLUSIONS

Modern structural and functional polymer materials, which are a set of micro- or nanostructures, have unique mechanical and thermophysical properties that allow them to be used in structures subject to various external influences. An important stage in the creation and use of these materials is the development of appropriate mathematical models to describe their behavior in a wide range of changes in the presence of external operating factors. First, this refers to models describing the thermokinetics of the process of destruction of polymer materials (in particular, polymer fibers) caused by the interaction of intense heat fluxes with solids: heating of materials by plasma flows, laser, or electron beams.

The mutual influence of micro- and macrostages of the process of destruction of polymer materials is mathematically described, its main parameters and limiting characteristics are determined, and a relationship is established between molecular constants characterizing the structure of a material and those characterizing macroscopic characteristics of strength. A generalized structural–kinetic theory of the destruction of polymer fibers under purely thermal action on cracked specimens is presented. The developed theoretical concepts of the thermokinetics of the process of thermal destruction of polymer fibers from the standpoint of the kinetic thermofluctuation concept make it possible to predict the thermal durability of a sample under its thermal loading. The obtained theoretical relations are of practical interest for the development of methods for localization, intensification, and control of the kinetics of crack growth in polymer materials.

Author's contribution

E.M. Kartashov – developing the theory for thermokinetics of the polymer fiber thermal destruction process from the standpoint of the kinetic thermofluctuation concept, research and derivation of formulas, and writing the text of the article.

The author declares no conflicts of interests.

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