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Kinetic Models for the Prediction of the Lifetime of Polymeric Materials

E.V.Deyun, G.B.Manelis, E.B.Polianchik, and L.P.Smirnov

Theoretical and experimental data for the degradation of polymers under the influence of mechanical stresses are surveyed from the standpoints of chemical physics. Kinetic models for the bulk-phase breakdown of polymers are examined and an approach is formulated to the prediction of the lifetime of articles made from polymeric materials.
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I. INTRODUCTION

One of the principal problems which the theory and practical applications of polymeric materials face as a result of progress in science and engineering is a quantitative prediction of the useful lifetime of polymeric materials and control of their stability[1]. The urgency of these problems is due to the expansion of the fields in which polymeric materials are applied, the wide variety of types of polymeric articles, the regimes and conditions under which they are employed, and the increase in the number of classes of polymers used; it is also associated with the need to solve problems involving ways of insuring the reliability of polymeric articles, the choice of the optimum polymeric material for a particular article, the design of a polymeric material, etc.

In technology, medicine, and other fields polymers are used mainly as constructional materials. The stability (lifetime) of a particular construction comprising a given polymer under specified conditions and operating regimes can be characterised by the time during which the article either breaks down or undergoes significant changes in its shape and dimensions, as a result of which the construction loses its suitability for the prescribed purpose. Problems of the stability of polymeric articles are considered below from the standpoint of their breakdown under the influence of mechanical forces.

The review does not deal with the characteristics of the breakdown of composite polymeric materials. Experimental and theoretical studies devoted to this problem are being published with an increasing frequency and their analysis requires a special survey.

II. THEORY OF THE BREAKDOWN OF SOLIDS

There is at present no unanimous view on the breakdown of solids, particularly polymers; there is therefore no generally accepted mathematical procedure whereby one could estimate quantitatively the strength characteristics, predict their changes during use, and determine the conditions under which breakdown occurs. It is possible to distinguish two main and to a large extent conflicting views on the breakdown process—static and kinetic[2-4].

The traditional view on the breakdown process is that breakdown is a critical event. In the mechanics of continuous media and in physical theories taking into account the atomic-molecular structure of bodies the static approach to the problem of strength involves the introduction of concepts of limiting states and ultimate strengths[3,5]. There is a whole series of theories of the limiting state, each of which is based on specific hypotheses concerning the breakdown condition. A common feature of all these theories is the claim that the breakdown of any body occurs when a certain function of the components of the stresses and deformation tensors or the deformation energy exceeds a specific quantity $C_{\lim}$, which is believed to be a fundamental physical constant of the given body[2,3,6]. In practice it is very often assumed that breakdown occurs if one of the principal stresses reaches its limiting value $\sigma_{\lim}$, which can be determined experimentally by testing a material for rupture on extension and under so-called standard conditions (at a specified constant temperature, pressure, and rate of deformation).[3,7] Together with $\sigma_{\lim}$, $\varepsilon_{\lim}$—the maximum deformation determined under standard conditions—is used as the ultimate strength[3,8].

The experimental studies of the breakdown of many materials established a series of facts indicating the kinetic nature of the process: it has been shown that the limiting characteristics ($\sigma_{\lim}$, $\varepsilon_{\lim}$) depend on the regime and conditions under which the tests are carried out (preliminary load, rate of deformation, and temperature)[7-10]; it has been established that the breakdown of a body occurs also following the application of stresses weaker than the ultimate strength $\sigma_{\lim}$; under these conditions, the weaker the stress the longer the lifetime of the specimen under load, until the instant of rupture t_r.[4,11-13] Systematic studies on hundreds of objects (inorganic salts, metals, alloys, polymers, and composite materials) established that the dependence of t_r on the temperature T and on the stress σ for materials of different chemical types is the same and can be described by the equation

$$t_r = t_0 \exp \frac{U_0 - \gamma\sigma}{RT}, \qquad (1)$$

where t_0, U_0, and γ are constants of the material.

Attempts to explain the conflict between the assumption of the critical nature of breakdown and the time dependence of strength and hence to develop a mathematical procedure which could take into account the fact that the breakdown is a function of time, whilst retaining the static approach, have been frequently made[14-18].

Thus the kinetic nature of the breakdown of polymers is frequently related to the characteristic features of the behaviour of polymeric materials, consisting in a significant alteration of their limiting characteristics as a function of time under the influence of heat, moisture, and many other factors[7,19-21]. The decrease of the limiting characteristics $C_{\lim}$ is usually defined as the ageing of the material and its increase is believed to be due to structure formation processes (crystallisation, orientation of macromolecules, etc). In the

prediction of the time corresponding to the breakdown of the polymeric structure within the framework of the static approach to breakdown, but with allowance for thermal ageing, the kinetic parameters describing the time variation of C_{lim} are usually determined experimentally by accelerated tests[7,22]. The method consists in maintaining specimens at elevated temperatures for specified periods without the application of mechanical stresses, this being followed by the determination of the limiting characteristics under standard conditions and by the calculation from the $C_{lim}(t)$ kinetic curves obtained, of the activation energy and the pre-exponential factor and the determination of the kinetic law of the reaction. When the results are extrapolated to the temperature range in which the given polymeric material is actually used, it is assumed that the characteristics of the variation of C_{lim} determined in the tests are maintained.

In order to describe the kinetics of the ageing and structure formation process, the combined graphical and analytical method[23,24] is used together with the mathematical procedure employed in describing the kinetics of chemical reactions[22,25], which, incidentally, is not justified from the theoretical point of view, because the relation between the limiting properties and the concentration of the chemical groups and bonds has not been established. The time of the breakdown of the object is determined in this approach as the time of attainment at any point in the construction of equality between C_{lim}, calculated for the operating conditions and regime for the given construction, and the value of this characteristic calculated in the analysis of the strained-deformed state of the construction under the given conditions (Fig.1). We emphasise that here one assumes in essence that the kinetics of the variation of the limiting characteristic $C_{lim}(t)$ are determined solely by the law governing the variation of the temperature $T(t)$ and are independent of the stress $\sigma(t)$.

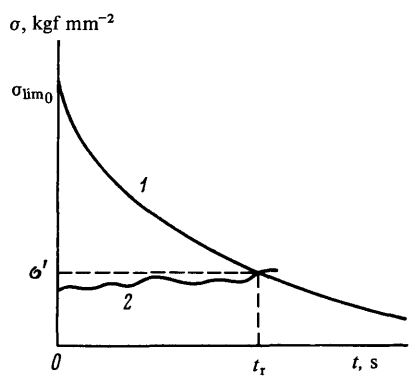


Figure 1. Scheme for the prediction of the breakdown time of a polymeric object taking into account the thermal ageing of the polymer: *1*) kinetic $\sigma_{lim}(t)$ curve for the given polymeric material under the operating conditions and regime of a specific construction; *2*) law governing the variation of the stress $\sigma(t)$ at a characteristic point for the given object under specified operating conditions and regime.

It can be shown that in this approach the activation energy for the breakdown process is equal to the activation energy for the ageing process E_{age} and is independent of σ, while the $t_r(\sigma)$ relation is much less pronounced than the relation described by Eqn.(1). Indeed, it is evident, for example, in the case of the variation of σ_{lim} during ageing in accordance with the first-order equation $\sigma_{lim} = \sigma_{lim_0}\exp(-kt)$, where $k = k_0\exp(-E_{age}/RT)$, that the relation $t_r(T, \sigma)$ should be described by the equation

$$t_r = \frac{\ln \lim 0/\sigma'}{k_0} \exp \frac{E_{age}}{RT}, \qquad (2)$$

where σ' is the stress at the instant of breakdown and σ_{lim0} is the ultimate strength of the initial "non-aged" material. Thus allowance for the thermal ageing of polymeric materials does not explain satisfactorily the inconsistency between the concept of breakdown as a critical, limiting event and the experimental time variation of strength described by Eqn.(1).

It has been suggested that the kinetic nature of breakdown be taken into account by introducing into Griffith's formula[26] for the ultimate strength of a solid with a crack of length l_{cr}, i.e.

$$\sigma_{lim} = [2wE/\pi(1-\nu^2)l_{cr}]^{0,5} \qquad (3)$$

the relation between Young's modulus E and the rate of deformation[14] or by replacing Young's modulus by the relaxation modulus $E(t)$ and taking into account the time variation of the cohesive energy of breakdown w.[15]

Detailed analysis of the time variation of the strength of solids and direct studies of the elementary reactions occurring in polymers subjected to a mechanical load led to the conclusion[4] that the time variation is not determined by the accompanying processes (such as the sorption of moisture[16], the redistribution of stresses in heterogeneous materials[17], etc.) but is inherent in the very mechanism of the breakdown. Experimental study of the $t_r(T, \sigma)$ relation together with theoretical ideas concerning the decrease of the energy barrier in the force field served as a basis for the creation of a kinetic theory of the strength of solids, which constitutes the second of the possible approaches to the breakdown process. According to this theory[4], the external mechanical force does not as a rule itself lead to the rupture of interatomic bonds; by deforming these bonds, it merely accelerates the breakdown process, reducing the activation barrier. The rupture of strained interatomic bonds takes place as a function of time under the influence of the thermal movement of atoms (thermal fluctuations).

III. KINETIC MODELS OF THE BULK PHASE BREAKDOWN OF POLYMERS

In a number of studies the kinetics of the bulk-phase breakdown of solids are described on the basis of a phenomenological approach[2,27-31]. Some investigators, for example, Il'yushin and Pobedrya[2] and Moskvitin[3], introduced the concept of the vulnerability of the material ω; the physical significance of the vulnerability is not defined, but it is assumed that during the breakdown process the ω increases from 0 to 1 and that on breakdown $\omega = 1$.

On the basis of general considerations, according to which the rate of change of vulnerability should increase with increase of σ and should tend to a maximum reached directly before macroscopic breakdown, it has been suggested that the kinetic equations for the vulnerability be formulated as follows[27,28]:

$$\frac{d\omega}{dt} = A\sigma^{\beta}/(1-\gamma\omega)^{p}, \qquad (4)$$

where A, p, β, and γ are constants.

Since it has been noted[2] that Eqn.(4) does not agree well with experimental data for $\sigma \neq$ const., it has been suggested[29] that a new parameter q, the rate of change of which is related to the rate of change of σ, be introduced into this formula.

The theory of long-term strength described in the monograph of Il'yushin and Pobedrya[2], introduces the concept of the vulnerability (susceptibility to damage) tensor $P(p_{ij})$ with the components

$$p_{ij} = \int_0^t \varphi_{ijkl}(t-\tau)\,\sigma_{kl}(\tau)\,d\tau, \qquad (5)$$

and it is suggested that in the absence of stresses during a time interval $0 \leq t \leq t'$ all the components of the tensor P are zero, i.e. the breakdown of a "non-ageing" material is considered.

Although breakdown is considered in the above and similar studies as a process developing as a function of time, its physicochemical nature is not taken into consideration. This is responsible for limitations in the employment of relations of this kind, which are characteristic of phenomenological theories[32].

Attempts have been made frequently to create a mathematical procedure for the description of the kinetics of breakdown which would be able to take into account adequately and physicochemical processes occurring in the solid when the latter is acted upon by external mechanical forces[4,33-45]. However, while postulating a particular dependence on temperature and applied stress of the probability of the breakdown of strained interatomic bonds, the authors of these studies confined themselves to determining the type of relation $t_r(t, \sigma)$; furthermore, they considered (with a single exception[46]) only simple kinetic schemes. In some of these studies arbitrary and sometimes contradictory assumptions were made: in particular, in formulating the expression for the rate of rupture of strained bonds at constant T and σ, account was taken of the dependence of this rate on the current concentration of the strained bonds, but the increased number of ruptured bonds was disregarded[41-43].

Together with the differential relations for the description of the bulk-phase breakdown, integral equations have also been proposed[4,47,48]. Thus, in predicting the lifetime of polymers on extension with time-dependent stress and temperature, the principle of the summation of the contributions to breakdown is used in the form of the relation

$$\int_0^{t_r} \frac{dt}{t_r[\sigma(t), T(t)]} = 1, \qquad (6)$$

called Bailey's integral. Eqn.(1) or the expression

$$t_r = B\sigma^{-b} \exp \frac{U_0}{RT}, \qquad (7)$$

proposed for the description of the lifetime of elastomers[12], is then used normally as the function $t_r(T, \sigma)$. However, it has been noted that, in this approach to the prediction of the useful lifetime of polymeric materials under load, the error is low only for a single application of a load with a complex relation $\sigma(t)$ and also for the application of a load for a small number of cycles[4,47,48]. It must be emphasised that the use of integral relations of type (6) for the description of the kinetic process under variable conditions, which determine its rate (particularly for the determination of t_r with $\sigma \neq$ const. or $T \neq$ const) is possible, according to the principal postulates of chemical kinetics, only when the rate of the given process is independent of the degree of completion of the process.

A sufficient amount of experimental data, demonstrating convincingly the common features of the mechanisms of different types of degradation of polymers, particularly mechanical breakdown and thermal degradation, has now accumulated. The application of modern physicochemical research techniques and comparison of the experimental relations governing mechanical breakdown and thermal degradation made it possible to show that, in polymers acted upon by stretching stresses, chemical reactions take place whose nature is identical to that of the reactions occurring in the thermal degradation of the polymers[4]. Thus, in many of the instances investigated, the activation energy for the mechanical breakdown of the polymer U_0 proved to be close to the activation energy for its thermal decomposition E_T[4,49-52]. The identity of the intermediate and final products of these processes has been observed[4,53-60] and it has been shown that the variation of the molecular weight distribution is identical[4,61-62]; the increase of the lifetime following the introduction of inhibitors and antioxidants[21,63-65] and the decrease of the lifetime after the addition of sources of free radicals[4,66,67] have been demonstrated.

Thus the mechanical breakdown of polymers can be regarded as a chemical reaction involving the dissociation of interatomic bonds subjected to a mechanical load and the rate of dissociation of the strained bonds is determined not only by the temperature and degree of reaction, as in thermal degradation, but also by the magnitude of the stretching stress. We may note that an analogous influence on the rate of the process is shown by mechanical stresses also for other types of degradation of polymers (hydrolytic[68-70], thermo-oxidative[71], and photothermal[4]). The mechanical initiation of chemical reactions in solids has been examined in a series of studies[72-75].

Thus, from the standpoint of chemical physics, the degradation of polymers is a multifactorial process, the rate of which depends on temperature, the action of various chemical agents (water, oxygen, etc.), irradiation, and mechanical stresses. Depending on the combination of these factors acting on the polymer, it is possible to distinguish thermal, thermo-oxidative, hydrolytic, photothermal, and other types of degradation, and among them different types of mechanical degradation of polymers (mechanothermal, mechanothermo-oxidative, mechano-hydrolytic etc.). In conformity with the foregoing, one can assume that mechanical stresses (and apparently also irradiation[76]) cannot alter the mechanism of the reactions involving the degradation of polymers and that the corresponding types of mechanical degradation include the same elementary stages as degradation in the absence of stresses; however, the ratio of the rates of the individual stages changes significantly under these conditions as a function of the active factors determined by external conditions. For example, mechanical stresses under the conditions of a radical chain degradation mechanism activate the chain initiation process and apparently, to a lesser extent, the chain propagation process. Accordingly, the rate of chain initiation is much higher as a rule in photothermal degradation than in thermal degradation of polymers.

Thus in the most general case the problem of predicting the lifetime of a polymeric object requires, firstly, the determination of the chemical mechanism of the degradation of the given polymer, and the elucidation of the set of elementary stages of the process and of the dependence of the rates of these stages on the temperature T and the stress σ, the irradiation intensity I, and the concentrations c_i of the possible reactants and reaction products, and secondly, the determination from the operating conditions and regime for the given object of the laws governing the variation of $T(t)$, $\sigma(t)$, $I(t)$, and $c(t)$ at the characteristic points of the object. The determination of the stability of the polymeric object

must be based on the solution of the appropriate equations for the degradation kinetics subject to the observed laws governing the time variation of T, σ, I, and c_i.

In the general case this problem is extremely complex; comparatively simple special cases of the problem have now been analysed[77-88]. In the analysis it was assumed that the influence of the mechanical field on the rate of reaction reduces to the alteration of the energy barrier to the dissociation of the interatomic bond E_0. We may note that calculations performed taking into account the interaction between the atoms with the aid of the Morse potential[44,89-91] established that the dependence of the energy barrier E on the tension f in the chemical bond is non-linear, but allows a linear fit within a comparatively wide range of values of f. Then, assuming that the load is uniformly distributed along all the bearing bonds and taking into account the fact that, for a constant σ, the accumulation of breaks in the bonds leads to an increase of the tension in the surviving bonds, one can write

$$E(\sigma) = E_0 - \alpha\sigma n_0/n, \qquad (8)$$

where n_0 is the initial concentration of the bearing bonds, n the current concentration of the bearing bonds, and α a coefficient determined by the nature and structure of the substance.

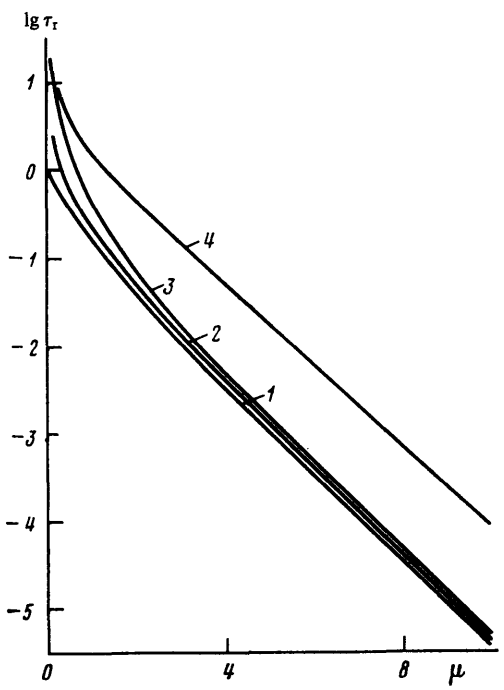


Figure 2. The lg $\tau_r(\mu)$ relation for $\phi(\Pi) = 1$ (curve *1*), $1-\Pi$ (curve *2*), $(1-\Pi)^2$ (curve 3), and $(1-\Pi)(0.01+\Pi)$ (curve *4*).[77,78]

In the case of a simple irreversible reaction, the rate of mechanical degradation at constant T and σ can be described by the following dimensionless equation[77-79]:

$$\frac{d\Pi}{d\tau} = \varphi(\Pi)\exp\frac{\mu}{1-\Pi}, \qquad (9)$$

where $\Pi = 1-n/n_0$ is the relative concentration of the broken bearing bonds (the degree of accumulation of defects), $\mu = \alpha\sigma/RT$ the parameter characterising the intensity of the mechanical field, $\phi(\Pi)$ the kinetic law governing the reaction, $\tau = ktn_0^{m-1}$ the dimensionless time, $k = k_0\exp(-E_0/RT)$ the rate constant for the chemical reaction, k_0 the pre-exponential factor, and m the order of the reaction.

Eqn.(9) can be readily integrated. The dimensionless lifetime τ_r (corresponding to $\Pi = 1$) is determined solely by μ and $\phi(\Pi)$, i.e. the dependence of $\tau_r(\mu)$ for the given type of $\phi(\Pi)$ is universal. The lg $\tau_r(\mu)$ curves plotted for different $\phi(\Pi)$ are non-linear for low values of μ and, when $\mu > 2$, they can be described with satisfactory accuracy by a linear equation (Fig.2), i.e. the following expression can be formulated in a dimensional form for the time variation in the region of high stresses ($\mu > 2$):

$$t_r = \frac{a}{k_0}\exp\frac{E_0 - b\alpha\sigma}{RT}, \qquad (10)$$

the expression being analogous to Eqn.(1). In the region where $\mu < 2$ the observed $\tau_r(\mu)$ relations are described satisfactorily by Eqn.(7). We may note that the deviation of the lg $t_r(\sigma)$ relation from linearity under the conditions of low stresses has been observed experimentally in all the cases investigated[4].

The $\Pi(\tau)$ kinetic curves are of the self-accelerating type regardless of the form of $\phi(\Pi)$ and it is possible to distinguish qualitatively two stages in the development of the process: at the beginning a comparatively slow increase in the concentration of the ruptured bearing bonds, proceeding almost at a constant rate, followed by a rapid "avalanche like" increase. The degree of accumulation of defects Π^* for which there is a transition from the slow to the rapid stage of the process diminishes with increase of the parameter μ. The kinetic curves for the formation of volatile products[92] and for the change in light transmission[93] in the mechanothermal degradation of polystyrene are identical in form to the $\Pi(\tau)$ curve for a simple irreversible reaction.

The rate of thermal degradation of polymers is frequently described by equations for *two simultaneous first-order reactions*, which can be accounted for by the presence in the initial polymer of kinetically non-equivalent so-called strong and weak bonds. the difference between the activation energies for the radical-chain thermal degradation involving initiation via the strong and weak bonds being capable of reaching from 1–3 to several tens kcal mol^{-1}, while the initiation of degradation via the rupture of weak bonds give rise to a conversion of the polymer up to 10–30%.[40-52,94-96]

The equations for the mechanothermal degradation in the case under consideration can be formulated in a dimensionless form in the following way[78,79]:

$$\frac{d\Pi_1}{d\tau} = (1-\Pi_1)\exp\frac{\mu_1}{1-\Pi},$$
$$\frac{d\Pi_2}{d\tau} = \varkappa(1-\Pi_2)\exp\frac{\mu_2}{1-\Pi}, \qquad (11)$$

where $\Pi_1 = 1-n_1/n_0$ is the extent of accumulation of defects in the strong bonds, $\Pi_2 = 1-n_2/n_0$ the extent of accumulation of defects in the weak bonds, $\tau = k_1 t$ the dimensionless time, $\varkappa = k_2/k_1$ a parameter equal to the ratio of the rate constants for the degradation of the weak and strong bonds, $\Pi = c\Pi_1 + (1-c)\Pi_2$ the overall extent of accumulation of defects, and c the fraction of the strong bonds.

For comparatively low values of $\varkappa$(~10), the $\Pi(\tau)$ curves do not differ qualitatively from the corresponding curves in the case of a single simple reaction. For $\varkappa > 10^2$–10^3, the kinetic $\Pi(\tau)$ curves have three sections: initially the rate of accumulation of defects gradually diminishes with time, then there is

a more or less low-slope section of the curve, and at the end of the process the accumulation of defects proceeds at a very high rate. The first stage is largely determined by the rupture of the weak bonds: hence the $\Pi_2(\tau)$ relation can be described by a first-order equation. The length of the low-slope section of the $\Pi(\tau)$ curve diminishes with decrease of c and, when $c < 1-\Pi^*$, the $\Pi(\tau)$ curve degenerates into one characteristic of the model with kinetically equivalent bonds. The lifetime τ_r is then determined by the kinetic parameters of the weak bonds.

For low values of κ, the $\lg \tau_r(\mu)$ relation for all values of the parameter c retains the same nature as in the case of a simple unidirectional reaction. When the fractions of the weak and strong bonds are approximately equal, then, for sufficiently high values of $\kappa(\kappa \geq 10^3)$, the relation becomes non-linear over a wider range of variation of the parameter μ and can be described by two linear sections, the slope of the linear section of the $\lg \tau_r(\mu)$ relation being higher for low values of μ than for high values of μ.

The hypothesis that the mechanothermal degradation is reversible has been put forward in connection with the discussion of certain characteristics of the variation of the lifetime of solids of different chemical types observed under the conditions of relatively small stresses and high temperatures[97]. Previously an analogous degradative recombination mechanism had been proposed to describe the so-called chemical flow of cross-linked elastomers[98]. For a reversible reaction, the rate of mechanothermal degradation can be described by the following dimensionless equation[78-81]:

$$\frac{d\Pi}{d\tau} = (1-\Pi)^{m_1} \exp\left(\frac{\mu}{1-\Pi}\right) - \frac{\Pi^{m_2}}{\kappa}, \qquad (12)$$

where $\tau = k' t n_0^{m_1-1}$ is the dimensionless time, $\kappa = k' n_0^{m_1-1}$. .$^2/k''$ a dimensionless parameter characterising the ratio of the dissociation (k') and recombination (k'') rate constants, and m_1 and m_2 are the orders of the bond dissociation reaction and of the reaction involving the recombination and rupture of bonds respectively.

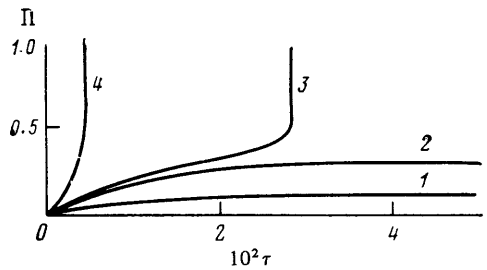


Figure 3. Kinetic curves for the accumulation of defects $\Pi(\tau)$ with $m_1 = 1$, $m_2 = 2$, $\kappa = 1.7 \times 10^{-3}$ and different values of μ: *1*) 2; *2*) 3; *3*) 3.1; *4*) 4.[78,79]

For this system, described by Eqn.(12), there exists a range of parameters μ and κ in which there is a possibility of a transition from a stationary to a non-stationary regime for a small change in external conditions, i.e., critical phenomena can arise. The specific form of the critical conditions $\mu_{cr} = \mu(\kappa)$ for specified pairs of values m_1 and m_2 can be readily found with the aid of Semenova's method. The nature of the $\Pi(\tau)$ curves changes sharply when μ passes through μ_{cr}: for $\mu < \mu_{cr}$, a stationary concentration of the ruptured bonds is established and there is no breakdown (the region of safe stresses); for $\mu > \mu_{cr}$, the process terminates with complete rupture of the bearing bonds (Fig.3). The influence of the reaction involving the recombination of the ruptured bonds on τ_r is significant only for values of μ slightly exceeding μ_{cr}: in this case the time taken to traverse a small (with respect to the values of Π) region, where the overall rate of breakdown is minimal, makes the main contribution to the lifetime of this specimen. For large values of μ (when $e^{\mu} \gg \kappa^{-1}$), the influence of the recombination of the ruptured bonds on the mechanothermal degradation becomes insignificant, and the $\tau_r(\mu)$ relation can be represented by Eqn.(10), obtained for a simple unidirectional reaction (Fig.4). We may note that the existence of safe stresses has been observed experimentally in the study of the mechanothermal degradation of cross-linked elastomers[99].

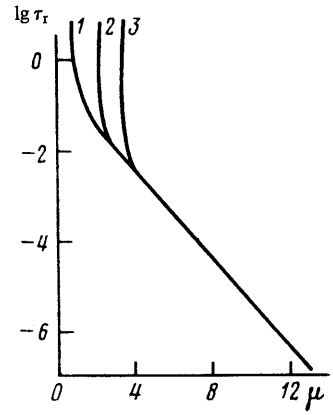


Figure 4. The $\lg \tau_r(\mu)$ relation with $m_1 = 1$, $m_2 = 2$, and different values of κ: *1*) 0.2; *2*) 10^{-2}; *3*) 10^{-3}.[78,79]

A radical-chain mechanism was proposed for the first time by Zakrevskii[46] in order to describe the kinetic characteristics of the breakdown of polymers. However, it dealt only with the initial stage of the process and no account was taken of the redistribution of the load on the surviving bearing bonds with increase of the number of ruptured bonds. The breakdown process proceeding via a radical-chain mechanism has been modelled in a number of studies[82-85]. The kinetic scheme for the process examined by Deyun et al.[83] includes the following stages: (1) the stress-activated initiation of the kinetic chain via the rupture of strained bonds in the macromolecules P_n, leading to the formation of terminal radicals R_t; (2) the depolymerisation of R_t as a result of the abstraction of the monomer P_2; (3) chain transfer in the interaction of R_t with P_n involving the formation of a central radical R_{ce}; (4) the stress-activated decomposition of R_{ce} with formation of R_t and molecules containing a double bond: (5) the migration of the free valence in R_{ce}, hindered by stresses, as a result of which R_{ce} is converted into R_t; (6) termination of the kinetic chain via the disproportionation or recombination of R_t.

Analysis of the corresponding kinetic equations using the method of quasi-stationary concentrations showed that, depending on the ratio of the parameters of the above equations, it is possible to distinguish three ranges of stresses

within the limits of which the $t_r(T, \sigma)$ relation is described by Eqn.(1) but with different values of U_0, t_0, and γ for each section, the values being complex combinations of the corresponding parameters of the elementary stages (see Table). A characteristic feature of the model of the breakdown of polymers under consideration is the establishment of quasi-stationary radical concentrations for relatively low stresses (regimes I and II); here the rate of mechanothermodegradation in regime I is limited by the decomposition of R_{ce} (stage 4), and that in regime II is limited by chain transfer (stage 3). For fairly large stresses (regime III), the radical concentrations are non-stationary throughout the process whose rate is determined by the initiation stage; thus in regime III the radical-chain process mechanism degenerates into a radical mechanism. The existence of the above three regimes in the mechanothermodegradation of polymers has been confirmed in a whole series of studies[62,100-107] and both types of breaks in the $\lg t_r(\sigma)$ relation, indicated in Fig.5, were noted. The presence of such breaks is usually attributed not to a radical-chain process mechanism but to the existence of a functional relation between the coefficient γ of Eqn.(1) and the temperature and stress due to the sharp alteration of the mobility of the side groups of the macromolecules[100,102].

Relation between the parameters of Eqn.(1) for the time variation of the strength and the constants of the elementary stages of mechanothermodegradation proceeding via a radical-chain mechanism*.[84]

Regime	U_0	t_0	γ
I	$\frac{E_{01}-E_{06}}{2}+E_{03}+E_{04}-E_{05}$	$\frac{(k_{06}/k_{01}P_0)^{0.5}RTk_{05}}{2^{1.5}k_{03}k_{04}n_0^{2.5}(0.5\alpha_1+\alpha_4+\alpha_5)\sigma}$	$\frac{\alpha_1}{2}+\alpha_4+\alpha_5$
II	$\frac{E_{01}-E_{06}}{2}+E_{03}$	$\frac{(k_{06}/k_{01}P_0)^{0.5}RT}{2^{1.5}k_{03}n_0^{1.5}\alpha_1\sigma}$	$\frac{\alpha_1}{2}$
III	E_{01}	$\frac{RT}{k_{01}n_0\alpha_1\sigma}$	α_1

*E_{0i}, k_{0i}, and α_i are respectively the activation energy, pre-exponential factor, and the structure-sensitive coefficient of the ith elementary stage and P_0 is the initial concentration of macromolecules.

The results of the calculation by the tabulated formulae of the values of U_0 and t_0 for a series of polymers [polyethylene, polypropylene, poly(vinyl chloride), polystyrene, poly(methyl methacrylate), and polyacrylonitrile], obtained using the literature values of the rate constants for the elementary stages of the thermal degradation of the corresponding polymers, in most cases agree satisfactorily with the experimental values of U_0 and t_0.[82] Thus the difference between the values of U_0 obtained in the study of the lifetime of the same polymer can be accounted for by the change in the rate-determining stages of mechanothermodegradation involving a radical-chain mechanism, when the stress is altered. In this connection one should note that comparison of the activation energies for thermal degradation and mechanothermodegradation (with the exception of regime I) is fairly conventional.

According to Regel' et al.[4], the quantity $t_0 = 10^{-12}-10^{-13}$ s for polymers, which is attributed to the period of the thermal vibrations of the atoms[108]. Thus the $t_r(T, \sigma)$ relation, defined by Eqn.(1), in essence involves only two constants (U_0, γ) characterising the polymer. However, the results of the analysis (see Table) have shown that such universality of the values of t_0 should not occur for mechanothermodegradation via a radical-chain mechanism. Indeed, for polymers listed above, calculation in the case of regimes I and III yields values of t_0 differing significantly from $10^{-12}-10^{-13}$ s. Apparently t_0 is frequently[4] assumed to be equal to 10^{-13} s in order to facilitate the calculation. One should also note that the use of the method of secants for the determination of t_0, recommended by Regel' et al[4], involves a long-range double extrapolation of experimental data on the logarithmic scale, which can also be a source of errors. These principles probably lead in many instances to the "pole redisplacement" effect[4].

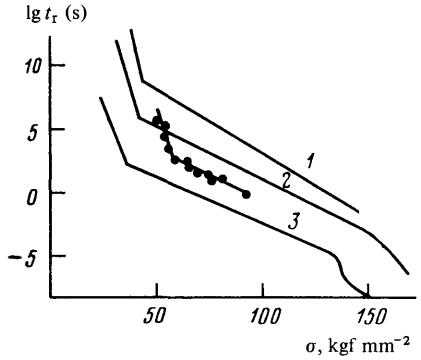


Figure 5. The $\lg t_r(\sigma)$ relation for polypropylene; calculation[84] using the tabulated formulae at different temperatures (K): *1*) 250; *2*) 300; *3*) 400. Circles—experimental data[4] at 300 K.

In the presence of a monofunctional stable radical In, termination of the kinetic chain is possible when In interacts with R_t or R_{ce}. It has been shown[85] that in this case there is a possibility of two regions in which inhibited and non-inhibited mechanothermodegradation develops, whose boundary is defined by the equation

$$[\mathrm{In}]^* = \frac{2(k_1k_6P_0\exp\mu)^{0.5}}{k_7+k_8k_7'/\left[k_4\exp\frac{\alpha_4\mu}{\alpha_1}+k_5\exp\left(-\frac{\alpha_5\mu}{\alpha_1}\right)\right]}, \qquad (13)$$

where k_7 and k'_7 are the rate constants for the interaction of In with R_t or R_{ce} respectively.

Depending on the ratio of the parameters of Eqn.(13), the critical concentration of the inhibitor [In]* either increases monotonically with increase of μ, passes through a minimum, or passes through a local maximum and then through a minimum. The nature of the [In]* (μ) curve determines the form of the relation $\lg \tau_r(\mu)$ (Fig.6). For given inhibitor concentration, there exists a maximum stress for which the inhibitor influences the breakdown process; starting from a certain inhibitor concentration, this test depends little on the latter. The qualitative nature of the theoretical $\lg t_r(\sigma)$ relation agrees with experimental data obtained in a study[62] of the breakdown of nitrocellulose in the presence of the 4-ethyl-4-hydroxy-2,2,6,6-tetramethylpiperidenyloxy-radical.

An analysis of the characteristics of the mechanothermodegradation taking into account the distribution of macromolecules with respect to chain lengths has been carried out[82] for a kinetic process mechanism involving the following stages: (1) initiation of the kinetic chain by the rupture of strained bonds in the macromolecules P_n* (n is the number of atoms in the chain of the macromolecule) with a rate constant k_1; (2) depolymerisation of the radical R_t with a rate constant k_2; (3) stress-activated chain transfer in the interaction of R_t with P_n involving the formation of R_{ce} and subsequent decomposition of the latter with a rate constant k_3; (4) termination of the kinetic chain via the disproportionation or recombination of R_t with a rate constant k_6. Unlike the kinetic degradation mechanism examined by Deyun et al[83], in this model the stages involving chain transfer and the decomposition of R_c have been combined into a single stage in order to simplify the calculation and the stage in which the free valence migrates is missing.

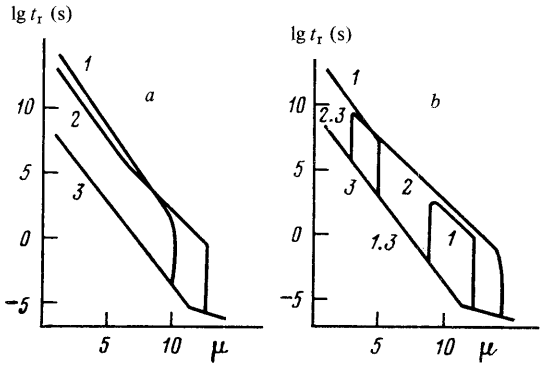


Figure 6. The lg $t_r(\mu)$ relation for the mechanothermodegradation of polymers in the presence of a monofunctional inhibitor[85] with $k_5/k_4 = 10^{10}$ and $\{k_1k_6[P_0]\}^{0.5}/k_7 = 5 \times 10^{-7}$: *a*) $k_3k'_7[P_0]/k_4k_7 = 10^4$ (curve *1*), 10^7 (curve *2*), and zero (curve *3*) and $[In] = 1.6 \times 10^{-4}$ (curve *1*), 1.6×10^{-5} (curve *2*), and zero (curve *3*); *b*) $k_3k'_7[P_0]/k_4k_7 = 10^7$ (curve *1*), 10^{10} (curve *2*), and zero (curve *3*) and $[In] = 10^{-5}$ (curve *1*), 2×10^{-7} (curve *2*), and zero (curve *3*).

The system of kinetic equations, formulated in accordance with the chosen reaction mechanism, agrees in broad outline with the system examined in the analysis of the thermodegradation of polymers[105]; the principal difference is that in mechanothermodegradation one takes into account the dependence of the rate of the initiation and chain transfer stages on the mechanical stresses. The system of equations has been converted into a dimensionless form by introducing the dimensionless time $\tau = k_1t$, the dimensionless concentrations of macromolecules $P_n(\tau) = \bar{P}_n(t)/\bar{P}_{n_0}(0)$ and radicals $R_n(\tau) = \bar{R}_n(t)/\bar{P}_{n_0}(0)$, and the dimensionless depolymerisation ($\kappa_2 = k_2/k_1$), chain transfer [$\kappa_3 = k_3\bar{P}_{n_0}(0)/k_1$], and chain termination [$\kappa_6 = k_6\bar{P}_{n_0}(0)/k_1$] rate constants ($n_0$ is the maximum number of atoms in the main chain of the macromolecule).

It has been shown that the kinetic curves for the variation of the overall concentration of radicals $R(\tau)$ are fairly complex (Fig.7). Radicals are initially accumulated at a decreasing rate; the subsequent shape of their $R(\tau)$ curves depends on the ratios of the parameter μ, κ_3, κ_6, and n_0. In a certain range of values of these parameters, it is possible to distinguish a section of the $R(\tau)$ curve along which the radical concentration remains virtually constant. The length of the quasi-stationary section is up to $(0.8-0.9)\tau_r$. The transition to the $R(\tau)$ curves without a quasi-stationary section takes place fairly abruptly as μ increases.

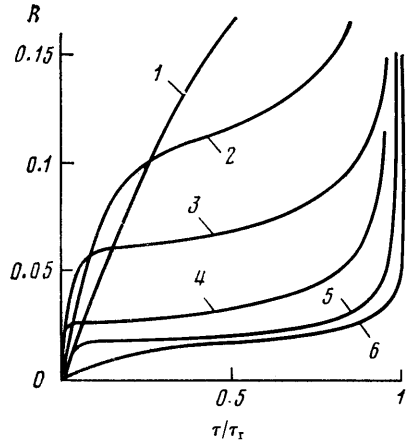


Figure 7. Kinetic curves for the variation of the overall concentration of free radicals $R(\tau)$ in the mechanothermodegradation of polymers by a radical-chain kinetic mechanism[84] with $n_t = 10$, $\alpha_3/\alpha_1 = 1$, $\kappa_2 = 10^2$, $\kappa_3 = 10$ (curves *1*–*5*) and 10^3 (curve *6*), $\kappa_6 = 10^6$ (curves *1*–*3*) and 10^8 (curves *4*–*6*), $\mu = 5$ (curves *1* and *4*–*6*), 4 (curve *2*), and 3 (curve *3*), and $n_0 = 100$ (curves *1*–*3* and *5* and *6*) and 200 (curve *4*) (n_t is the number of non-loaded atoms in the terminal sections of the main macromolecular chain).

The calculated $R(\tau)$ curves agree satisfactorily with the experimental characteristics of the accumulation of radicals in mechanothermodegradation[4,110]. The form of the calculated kinetic curves $P_n(\tau)$ depends on n; if n is small, then the induction period for the corresponding $P_n(\tau)$ curve is most distinct and the entire change in the concentration of the given product takes place virtually near the time of attainment of the maximum concentration P_n, which depends little on the process parameters and is largely determined by the value of n. We may note that the yield of the monomer $P_2(\tau_r)$ decreases with decrease of the parameter κ_2 and with increase of μ and κ_3. In the case of chain termination by the recombination of R_t the decrease of the number-average molecular weight $\bar{M}_n$ proceeds at a constantly increasing rate for all values of the parameter μ. On the other hand, if chain termination takes place via the disproportionation of R_t, then only for fairly large values of μ do the $\bar{M}_n(\tau)$ curves have the same form as in the previous case. For low values of the parameter μ, the kinetic curves $\bar{M}_n(\tau)$ have three sections: along the first and third sections $\bar{M}_n$ decreases at a gradually increasing rate, while along the second section the rate falls (Fig.8). The form of the kinetic $\Pi(\tau)$ curve is analogous to that of the $\bar{M}_n(\tau)$ curves.

IV. THE ROLE OF THE MECHANICAL MODEL IN THE KINETIC THEORY OF STRENGTH

The results of the analysis of certain kinetic models of the bulk-phase (quasi-homogeneous) breakdown, occurring over a wide range of conditions and regimes in the breakdown of polymers which are of practical importance, were examined above. Any theoretical model proposed to describe the breakdown kinetics involves (explicitly or implicitly) certain assumptions concerning the mechanical picture of the processes occurring in the loaded material, since each step involving the rupture of an interatomic bond constitutes at the same time a step in the rearrangement of the microstructure of the material.

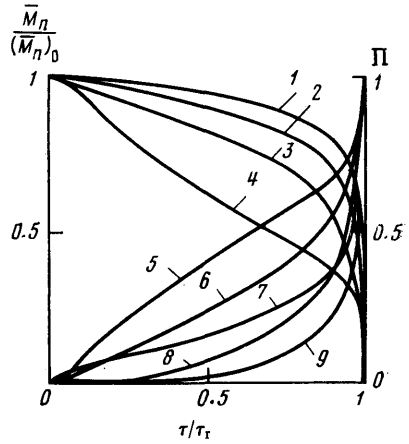


Figure 8. Kinetic curves for the variation of the number-average molecular weight (curves *1–4*) and for the degree of accumulation of defects (curves *5–9*) in the mechanothermodegradation of polymers by a radical-chain kinetic mechanism[84] with $n_t = 10$, $\alpha_3/\alpha_1 = 1$, $\kappa_2 = 10^2$, $\kappa_3 = 10$, and $\kappa_6 = 10^6$ (curves *1–5* and *7–9*) and 10^8 (curve *6*), $\mu = 3$ (curves *3–5* and *7*), 6 (curves *2, 6,* and *8*), and 9 (curves *1* and *9*), and $n_0 = 100$. The kinetic chain is terminated via recombination (curves *1–3, 5, 6, 8,* and *9*) and disproportionation (curves *4* and *7*).

Breakdown models, in which it is suggested that breakdown takes place throughout the bulk of the specimen, that the strength characteristics of the bonds are identical, and, in addition, that in most of the models mentioned above the load applied to the ruptured bonds is redistributed uniformly among the surviving bonds, have been examined in Refs. 33 to 45, 77–85, and others. Next it is assumed that the probability dp_i of the rupture of a bond under the influence of a force f_i during a time interval dt is described by an equation of the Arrhenius type:

$$dp_i = k_i \exp\left(-\frac{U_0 - \alpha f_i}{RT}\right) dt. \qquad (14)$$

Together with these models, others have been proposed[86,111] in which the non-equivalence of the chains with respect to strength characteristics and their non-uniform loading were assumed, but it was also postulated that the distribution of the load applied to the ruptured bonds among the residual surviving bearing bonds is uniform.

In particular, the influence of the non-uniformity of the load applied to the bonds on the kinetics of mechanothermodegradation was taken into account[86] subject to the following main assumptions: (1) throughout almost the entire lifetime of the specimen under load, the material remains linearly elastic; (2) a dimensionless parameter $x \geq 0$ can be assigned to each bond in such a way that all the strength characteristics (i.e. elastic constants and the parameters of the degradation kinetics) are functions of x and not of the time t; (3) the rupture of the bonds is described by the equation for an irreversible first-order reaction:

$$\dot{H}(x, t) = -H(x, t) k_0(x) \exp\{-[U_0(x) - \alpha(x)\Omega]/RT\}, \qquad (15)$$

where $H(x, t)$ is the density of the distribution of bonds with respect to x and Ω is the force acting on the bond.

If the rigidity of the bond is $\phi_1(x)$, then the stretching stress in the cross-section of the specimen is

$$\sigma(t) = \int_0^\infty H(x, t) \varphi_1(x) \varepsilon_{33}(t) dx, \qquad (16)$$

where ε_{33} is the elongation of the specimen.

Eqns. (15) and (16) can be written as follows in a dimensionless form:

$$\dot{h}(x, \tau) = -h(x, \tau) \varkappa(x) \exp[\omega(x) \varepsilon(\tau)], \qquad (17)$$

$$\mu(\tau) = \varepsilon(\tau) \int_0^\infty h(x, \tau) \varphi(x) dx, \qquad (18)$$

where $\tau = tk_0 \exp(-\tilde{U}_0/RT)$ is the dimensionless time, $\mu = \alpha\sigma/N_0RT$ the average dimensionless tension in the bonds, $h(x, \tau) = H(x, t)/N_0$ the relative density of the distribution of bonds with respect to the parameter x, $\varkappa(x) = k_0(x)\exp.(\tilde{U}_0/RT)/\tilde{k}_0 \exp[U_0(x)/RT]$ the dimensionless breakdown strengths for thermal degradation, $\phi(x) = \phi_1(x) = \phi_1(x)N_0/A$ the dimensionless rigidity of the bonds, $\varepsilon = \varepsilon_{33}A/N_0RT$ the dimensionless deformation of the specimen, $\omega(x) = \Omega_1(x)RTN_0/A\tilde{\alpha}$ the dimensionless decrease of the activation energy, $\Omega_1(x)$ the decrease of the activation energy corresponding to $\varepsilon = 1$, N_0 the initial number of bonds in the given cross-section $\tilde{U}_0$, $\tilde{k}_0$, and $\tilde{\alpha}$ are certain characteristics of U_0, k_0, and α respectively, $A = \int_0^\infty H(x, 0)\phi_1(x)dx$, and $\int_0^\infty h(x, 0)\phi(x)dx = 1$.

Eqns. (17) and (18) make it possible to deduce the expression

$$\mu(\tau) = \varepsilon(\tau) \int_0^\infty h(x, 0) \varphi(x) \exp\left\{-\varkappa(x) \int_0^\tau \exp[\omega(x)\varepsilon(\tau')] d\tau'\right\} dx, \qquad (19)$$

which fully describes the evolution of a specimen for an arbitrary law governing the deformation or the application of a load. The study of Eqn. (19) showed that, for a constant load at fairly high values μ (in the sense that $e^\mu \gg 1$), we obtain

$$\tau_r = \tau_0 \exp(-\rho\mu), \qquad (20)$$

where $\rho \gg 1$, i.e. a non-distribution of the load among the bearing bonds leads to a decrease of the lifetime compared with a uniform distribution; at the same time, the $\tau_r(\mu)$ relation remains exponential.

The calculated evolution of the distribution function $h(x, \tau)$ reflects qualitatively the course of the breakdown process observed experimentally[4,112]. The shape of the $\varepsilon(\tau)$ creep curves for high values of μ depends on the form of the function $h(x, 0)$ (Fig. 9). If $h(x, 0)$ has a rectangular shape, then the $\varepsilon(\mu)$ curves consist of two sections, while in other cases they have three sections. For low values of the parameter μ, the creep curves cease to depend on the form of $h(x, 0)$;

in this case the decrease in the number of bearing bonds in consequence of purely thermal degradation makes a major contribution to the development of creep. The $\Pi(\tau)$ curves are similar in form to the $\varepsilon(\tau)$ curves. For high values of μ, the lifetime is determined by the rupture of a relatively small number of bearing bonds. The decrease in the rate of increase of the concentration of broken bonds for low values of μ is related to the decrease in the total number of bonds as a consequence of thermal degradation.

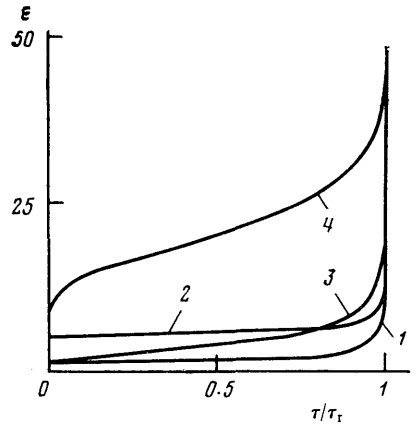


Figure 9. Creep curves $\varepsilon(\tau)$ for a non-uniform loading of the bearing bonds in mechanothermodegradation[86] with $\mu = 1$ (curve *1*), 5 (curve *2*), 1.2 (curve *3*), and 6 (curve *4*). The $h(x,0)$ curves *1* and *2* have a rectangular shape; the $h(x,0)$ curves *3* and *4* correspond to oriented capron[4,112].

One of the principal features of the mechanothermodegradation of real bodies is that the process as a rule develops initially as a homogeneous reaction, while in the concluding stage it is localised and terminates by the growth of a crack right through the specimen. Although the model discussed above and similar models[39,113] make it possible to explain qualitatively a whole series of features typical for mechanothermodegradation, they nevertheless do not provide an answer to the question which of the elementary steps in the breakdown process constitute the macroscopic breakdown of the given body[4,114] The initiation of a crack from single breaks, occurring on average uniformly throughout the bulk of the specimen, has still not been investigated. The study of the conditions under which the interaction of closely spaced continuity microdefects (bond breaks, submicrocracks) is significant and of the conditions under which breakdown occurs as a result of the growth of a single microdefect is complicated by the lack of effective solutions for the distributions of stresses and deformations in the vicinity of microdefects with allowance for the kinetics of the accumulation of microdefects and for the real structure of the polymer. The solution of the problem of the localisation of breakdown should, in principle, yield also an answer to the question how justified is the assumption, used in models describing quasi-homogeneous breakdown, that the transition from the bulk-phase breakdown to the growth of a crack right through the specimen coincides with a sharp increase of the rate of accumulation of defects.

In this connection mention should be made of the study[115] of the statistics of an *ensemble* of microdefects, the probability of the formation and growth of which depends on the local stresses in accordance with Eqn.(14). However, one then uses the solution of the problem of the distribution of stresses for an infinite crack extrapolated to the region of the typical dimensions of the microdefect. The same can also be said of a study[116] whose results are largely a repetition of those of the previous investigation. A direct solution of this problem by modelling the breakdown process using the Monte Carlo method on a computer has been attempted[117].

Several models, for instance[87,88,118-121], have been proposed to describe the kinetics of the growth of cracks right through the specimen. In most of these investigations the solutions of the theory of elasticity for a crack (section) through a continuous body were used together with particular assumptions whereby the specific features of the solution near the end of the crack (infinite stresses) can be eliminated. A correct formulation of the mechanical problem concerning the equilibrium governing the crack (it is assumed that a slowly growing crack corresponds to mechanical equilibrium) requires an explicit introduction of a parameter having the dimensions of length, i.e. it is necessary to invoke hypotheses concerning the structure of the material[118-121]. Together with the details of the structure of the material, the description of the kinetics of the growth of a crack right through the specimen requires the formulation of the kinetics of the elementary processes involving the rupture of interatomic bonds near the end of the crack, where, by virtue of the marked dependence of the rate of the process on the stresses, the breakdown is localised[87,88].

Thus the problems of the micromechanics of breakdown cannot be eliminated from kinetic models for the breakdown process. The attempts to disregard the structure of the material lead to implicit hypotheses concerning the structure[122] or the treatment remains open-ended[123].

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A theoretical relation has been established for different kinetic degradation schemes[77-88] between the lifetime in mechanothermodegradation and the parameter μ characterising the intensity of the mechanical field. Comparison of the results of the calculation showed that the $\lg \tau_r(\mu)$ relations obtained are qualitatively the same in the region of small values of μ, although they differ quantitatively. For sufficiently large values of μ, the relation between the logarithm of the lifetime and the applied stress can be represented by a single straight line, i.e. can be described by Eqn.(1) only for a simple reaction mechanism. As a result of the occurrence of two parallel reactions, the above relation is in some cases represented by two linear sections over a wide range of stresses. For a radical-chain kinetic mechanism of the degradation process, the dependence of the logarithm of the lifetime on the stress is most complex and, with the exception of the initial section, is represented in the general case by three linear sections, the ratios of the slopes of which are 5 : 1 : 2 (when the structure-sensitive coefficients of the elementary stages are equal). For a reversible reaction, critical phenomona are possible in mechanothermodegradation, and the range of "safe" stresses is determined by the ratio of the rate constants for the forward and reverse reactions. The non-uniformity of the distribution of bonds with respect to tensions leads to a decrease of the lifetime without altering the general form of the $\lg \tau_r(\mu)$ relation.

The results of the theoretical analysis[77-88] agree with experimental data, which makes it possible to employ the mathematical procedures developed in the above studies for the prediction of the useful lifetimes of polymeric articles. The problem of the prediction of the stability of polymeric articles can be simplified in the case of a complex radical-chain mechanism and the prediction itself can be made more exact. Theoretical analysis shows that in this case one must employ in calculations of the lifetime not the rate constants for the individual elementary stages of the degradation process, which are as a rule still not known with adequate accuracy, but the corresponding functions of the above constants, in terms of which the parameters of the mechanothermodegradation equations are expressed. The functions of the constants can be determined with the necessary accuracy from experimental lifetimes of polymeric materials. In extrapolating the results thus obtained to the operating conditions of the corresponding polymeric article, it is, however, necessary to bear in mind that when the kinetic mechanism of the degradation process is complex, the combination of elementary constants determining the macroscopic parameters of the mechanothermodegradation (U_0, t_0, γ) varies with the applied stress.

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Division of the Institute of
Chemical Physics, USSR Academy
of Sciences, Chernogolovka,
Moscow Region