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Prediction of the Variation of the Properties of Polymeric Materials after Prolonged Storage and Use

B.D.Goikhman and T.P.Smekhunova

The fundamental problems of the prediction of the changes in the properties of polymeric materials (in consequence of ageing, mass transfer, and the application of stresses) after prolonged storage and use are examined. The experimental conditions and the methods of interpretation of experimental data as well as characteristics of the method of accelerated tests on articles made from polymeric materials are discussed.
The bibliography includes 66 references.

CONTENTS

I. Introduction 748
II. The equivalent temperature as a characteristic of natural climatic conditions under which articles are stored and used 749
III. Changes in the properties of polymeric materials on ageing 750
IV. Changes in the properties of materials due to mass transfer processes 753
V. Prediction of the lifetimes of materials 754
VI. Accelerated tests on articles made from polymeric materials 755

I. INTRODUCTION

The increasing application of polymeric materials (PM) in various branches of the National Economy and the necessity to optimise their properties have given rise to the problem of improving the accuracy in predicting the duration of the technical suitability of the relevant articles.

On storage and during use, articles made of polymeric materials are acted upon by various factors: temperature, moisture, oxygen, ozone, light, radiation, corrosive media, biological factors, and applied forces. Depending on the duration and intensity of the influence, these factors lead to reversible and irreversible physicochemical processes, which include the following:

(a) thermal, radiation-induced, and light-induced ageing (chemical degradation and structure formation reactions, structural rearrangements at a supermolecular level), leading to irreversible changes in the properties of the polymeric material.

(b) Phase transformations in the polymeric material, which give rise to reversible changes in its properties.

(c) Mass transfer (relative migration of plasticisers in various elements of the articles, the removal of volatile components, the diffusion of moisture, etc.), causing changes in various properties of the articles.

(d) The accumulation of defects in the articles (constructions) owing to stresses active during storage and use, which lead to an alteration of the properties of the polymeric material, a change in its geometry, and the breakdown of the integrity of the constructions.

The influence of the above environmental factors on the polymeric material must be considered in terms of interrelations between them. For example, the simultaneous influence of heat, oxygen, and moisture gives rise to thermo-oxidative degradation (structure formation) in the material and hydrolytic degradation via different types of bonds, which is the reason for the complex variation of the properties of the polymeric material. The reversible and irreversible processes occurring in the polymeric material under the influence of the environment can be greatly accelerated if the articles are in a strained-deformed state.

In the problem of the estimation of the capacity for retention of the operational characteristics of the given articles the direct and converse tasks are distinguished. The direct task consists in estimating the storage times of the articles in terms of the permissible changes in their operational characteristics. The converse task consists in determining the required level of operational characteristics of the given articles to ensure their usability during a specified time. Formally, both problems are solved on the basis of the following condition:

$$Y_j(0)\rho_j(t) \geqslant [Y_j], \qquad (1)$$

where $[Y_j]$ and $Y_j(0)$ are respectively the maximum permissible and the initial characteristics of the article and $\rho_j(t)$ is the coefficient of the change in the characteristic Y_j with time (relative to the initial value).

The index of reliability, taking into account the sum total of the operational characteristics of the articles, is a generalised characteristic of the usability of the given articles. In view of the variation in the characteristics of the materials with time and the accumulation of defects in the articles under the influence of external conditions, the reliability index is a function of the storage time or the time during which the given articles are used. If this function has been determined quantitatively, the storage time can be found as the time required to attain the limiting permissible level of reliability; on the other hand, if the storage time has been specified, then the level of change in reliability can be determined from the above relation. In other words, in this case the problem also reduces to the solution of Eqn.(1), in which Y_j is the reliability index and $\rho_j(t)$ is the coefficient of its time variation. Here one should note that a certain excess reliability of the article at the beginning of the storage time is an inevitable "advance contribution" necessary to ensure the usability of the article within the limits of the specified time.

The correct solution of the kinetic problem of reliability involves considerable difficulties in most cases. For this reason, the following approach has come to be widely used in engineering practise. Eqn.(1) is solved for each of the characteristics which determine the usability of the article. To ensure the specified useful lifetime, the standardised requirements to be met by the characteristics are specified taking into account their time variation.

A characteristic feature of the problem of predicting the changes in the properties of a polymeric material is the short duration of laboratory tests at the stage involving

the development of the articles, i.e. under conditions where no direct experience in the use of the article can be gained. The problem can only be solved on the basis of the laws of chemical and physical kinetics and thermodynamics.

The majority of studies devoted to the prediction of changes in the operational properties of polymeric materials are characterised by an endeavour to simplify to the maximum possible extent the methods of interpretation of the kinetic $Y_j(t)$ curves. This frequently leads to the unjustified exclusion from consideration of a number of processes and hence to errors in prediction. This review deals with a series of practically most important aspects of the problem of prediction of the changes in the properties of polymeric materials on prolonged storage and use.

II. THE EQUIVALENT TEMPERATURE AS A CHARACTERISTIC OF NATURAL CLIMATIC CONDITIONS UNDER WHICH ARTICLES ARE STORED AND USED

In terms of thermal and other natural influences, the territory of the USSR can be divided into zones of cold, temperate, and hot climates. The climatic regions of the USSR differ considerably in terms of temperature, relative humidity, intensity of solar radiation, and other factors[1]. For example, the average diurnal temperature varies in the range from −50° to +40 °C, the hourly temperatures range from −60° to +45 °C, the maximum daily temperature amplitudes range from 20° to 30 °C, the average annual relative humidity is between 40 and 75%, the overall solar radiation intensity is between 87.7 and 158.5 kcal cm^{-2}, and the annual atmospheric precipitation ranges from 202 to 2788 mm.

The temperatures at which articles are stored, which in many respects determine the intensity of physicochemical processes, are particularly important. Furthermore, in many instances a change in the temperature of ambient air leads to the appearance and stresses in the articles (for example, diurnal variations in temperature induce non-stationary temperature stresses, while seasonal variations give rise to stationary stresses when there is a difference between the coefficients of thermal expansion of the constructional elements).

Variation of the temperature of ambient air during the storage of the articles within wide limits (up to 100 °C) makes it necessary to take into account the non-isothermal conditions in predicting the properties of the materials. The solution of kinetic equations under the conditions of a non-stationary temperature field may be carried out on a computer using the known laws governing the variation of temperature with time[2].

One of the ways in which non-stationary temperature conditions can be taken into account involves the introduction of the so-called equivalent temperature[3,4]. This term is understood as a conventional constant temperature at which the same changes take place in the given material during the time under consideration as under non-stationary temperature conditions. For chemical reactions described by the relation

$$\frac{dc}{dt} = -A_0 \exp\left(-\frac{U}{RT}\right) f(c) , \qquad (2)$$

where c is the concentration of the reactant, U the apparent process activation energy (in the general case the temperature coefficient of the rate of the process), A_0 the pre-exponential factor, R the gas constant, and f(c) a function independent of temperature, the present authors[4] found an

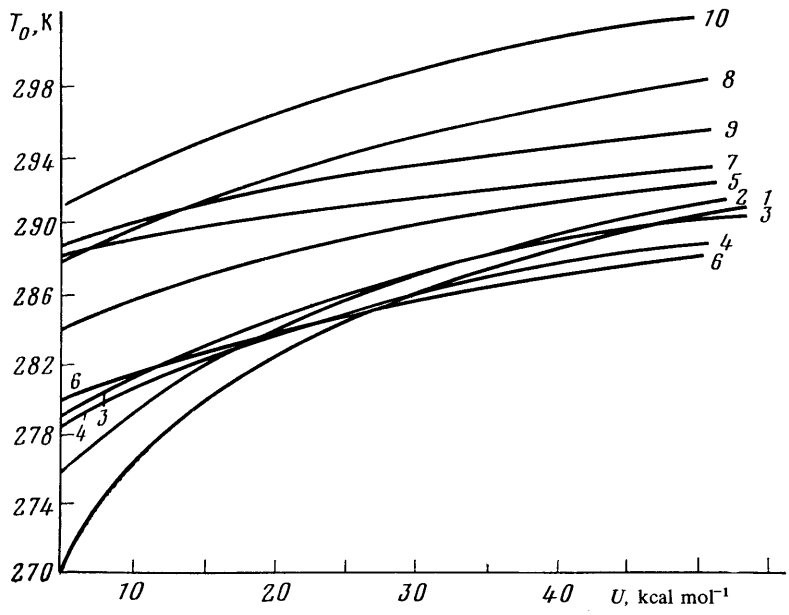


Figure 1. The $T_0(U)$ relation for representative points according to the results of observations carried out at specified times in different climatic regions: 1) very cold; 2) cold; 3) moderately cold; 4) moderately cold and moist; 5) moderately warm; 6) moderately warm and moist; 8) hot and dry; 9) moderately hot and moist; 10) very hot and dry.

expression describing the equivalent temperature:

$$T_0 = -\frac{U}{R}\left\{\ln\left[\frac{1}{t_0}\sum_{j=1}^{n}\Delta t_j \exp\left(-\frac{U}{RT_j}\right)\right]\right\}^{-1}, \qquad (3)$$

where n is the number of intervals Δt_j with an average temperature T_j during the time interval t_0 under consideration.

This expression for the equivalent temperature was obtained for decomposition processes, creep, the relaxation of stresses, etc.[4] The identity of the expressions for the equivalent temperature is due to the fact that the temperature dependence of the rates of different chemical and physical processes is described by analogous relations of the Arrhenius type.

It follows from Eqn.(3) that the equivalent temperature is a function of the apparent process activation energy and of the distribution of temperatures. For a known distribution of temperatures, the dependence of T_0 on U can be calculated beforehand. Fig.1 presents plots of T_0 against U calculated by Eqn.(3) for different climatic zones in the USSR using data from Ref.1†.

One should note that the equivalent average temperatures are not the same and in many cases there is not even a qualitative correlation between them. For example, the average annual temperature in the zone of the temperate, warm, and moist climate is 6.0 °C, while in the zone of the very cold climate it is −12.5 °C.[1] For the same climatic zones, the equivalent temperatures for $U = 35$ kcal mol^{-1} are respectively 13.3° and 14.3 °C (Fig.1), i.e. a higher equivalent temperature corresponds to a lower average annual temperature. Therefore treatment based on average annual temperatures can lead to significant errors in calculations in view of the considerable dependence of the rates of the processes on temperature.

The equivalent temperature found from Eqn.(3) can be regarded not only as the extrapolation temperature in predicting the changes in the properties of materials but also as a generalised characteristic of the temperature conditions in the storage and use of materials. It follows from the $T_0(U)$ relations in Fig.1 that the values of T_0 for different climatic zones are significantly different (up to 20 °C). In view of the significant dependence of the rates of processes on temperature, a difference of 3–4 °C in the equivalent temperature leads to a considerable difference in the rates of processes and the storage time.

The Table presents the values of T_0 and the relative rates (w/w_{cold}) of physicochemical processes in different climatic zones of the USSR. The rate of processes in the zone of the cold climate (w_{cold}) has been adopted arbitrarily as unity. Evidently the rates of physicochemical processes in different climatic regions can differ severalfold. Nevertheless the specified storage and utilisation times for articles are as a rule stated to be the same for the entire territory of the USSR (they are calculated for the most severe conditions). After this time has elapsed, the stock of given articles can differ severalfold depending on the storage conditions.

† In the absence of data on the distribution of temperature in the given climatic region, the equivalent temperature can be estimated from average minimum and maximum monthly temperatures[5]. The distribution of temperature on the surface and in the bulk of the articles differ somewhat from the distribution of temperature in the ambient air. In the absence of the effect of solar radiation, the corresponding values of T_0 will be lower than those in Fig.1.

Bearing in mind that the zone of the dry, hot climate constitutes only ~10% of the territory of the USSR (the zones of the cold and temperate climates constitute 67 and 23% of the territory of the USSR respectively)[1], the desirability and economic efficiency of differentiating the storage times as a function of temperate conditions, at least for large and expensive articles used under the conditions of a single climatic region, becomes evident.

The relative rates of processes in different climatic regions of the USSR.

Climatic region	U = 15 kcal mol^{-1}		U = 25 kcal mol^{-1}		U = 35 kcal mol^{-1}	
	T_0, K	w/w_{cold}	T_0, K	w/w_{cold}	T_0, K	w/w_{cold}
Cold	281.9	1.0	285.6	1.0	288.3	1.0
Moderately warm	287.0	1.58	289.0	1.65	290.6	1.7
Dry and hot	291.2	2.46	294.0	3.5	296.0	4.8

III. CHANGES IN THE PROPERTIES OF POLYMERIC MATERIALS ON AGEING

The experimental methods for the prediction of the changes in the properties of polymeric materials during ageing are based on accelerated tests under conditions of increased temperature, moisture concentration, oxygen, radiation intensity, stresses, etc.

A survey of studies[6–16] during recent years in the Soviet literature shows that the curves describing the variation of the characteristics of materials during ageing under forced conditions are complex. Nevertheless, the authors of these studies used simplified methods for the interpretation of experimental kinetic curves in calculating the expected changes in the properties of materials or their storage times. This approach can lead to contradictory estimates of the expected changes[10] and also, as will be shown below, to not only quantitative but also qualitative errors. This leads in its turn to errors in the determination of the times of technical suitability of articles or unjustifiably high specifications which must be met by the operational characteristics.

In the general case the characteristic of a material investigated can be expressed in the form

$$Y_j = f_i(c_1, c_2, \ldots, c_n), \qquad (4)$$

where Y_j is the characteristic of the material under consideration and c_i the concentration of bonds of the ith type (chemical, physical) which determine the level of Y_j.

The time variation of the characteristic Y_j is evidently determined by the law governing the variation of concentration:

$$c_i = c_i(t, T, \xi), \; i = 1, 2 \ldots n \qquad (5)$$

(here t is the time, T the temperature, ξ the stress, radiation dose, the concentration of oxygen, etc.).

When the mechanism of ageing, which determines the form of function (5), and the law governing the establishment of properties (4) are known, the relation $Y_j = f(t, T, \xi)$ is unambiguously defined and the problem of prediction reduces to the corresponding analytical calculations at the storage and operating temperatures of the material. This in turn indicates the need to investigate and determine the quantitative relations between the rate of ageing and different factors. The determination of the mechanism of ageing and the

law governing the establishment of properties would be the best guarantee of a reliable prediction.

However, in most cases the investigator does not have the necessary information concerning the structure of Eqns.(4) and (5) and the corresponding kintic constants. The generally accepted approach therefore consists in the study of the kinetics of the variation of the characteristics of the material under investigation $Y_j(t, T)$ with subsequent extrapolation of the results to the real temperature conditions.

We shall analyse the possible features of the variation of the characteristic $Y_j(t)$ (for example, in thermal ageing). We shall assume that relation (4) can be represented by the fairly general expression

$$Y_j = \sum_{i=1}^{n} \alpha_{ji} c_i^{m_{ji}}, \qquad (6)$$

where α_{ij} and m_{ji} are coefficients.

It follows from Eqns.(5) and (6) that, even under the conditions of simple kinetic laws governing the variation of the concentrations of bonds, the Y_j characteristic varies with time in a complex manner. The identity of the kinetic laws governing the variation of Y_j and c_i in terms of relative units obtains only for $n = 1$ and $m_{ji} = 1$ (in this case the kinetic parameters of the changes in the above quantities are identical). For $n = 1$ and $m_{ji} \neq 1$, the kinetic parameters of the variation of the bond concentration and of the characteristic are not identical even in the simple case where the bond concentration varies in accordance with the first-order law. For $n = 2$ and $m_{ji} = 1$, the above kinetic parameters also differ.

The different operating characteristics of the material are different functions of the concentration of the same bonds. In other words, the coefficients of Eqn.(6) for different characteristics of the material can be different. Therefore the same chemical and physical transformations in the material can lead to different changes in particular operating characteristics. The kinetic parameters of the variation of different characteristics can therefore also differ. In particular, the apparent activation energy U—the temperature coefficient of the rate of change of the characteristics—may not be the same as the true activation energy for the physicochemical process. The presence of stable bonds and the occurrence of recombination processes lead to a limiting value of the characteristic Y_j^{∞}.

For parallel competing first-order processes (structure formation and degradation) with $n = 2$ and $m_{ji} = 1$, we have

$$c_1 = c_1^0 \exp(-k_1 t); \quad c_2 = c_2^{\infty} - (c_2^{\infty} - c_2^0) \exp(-k_2 t) \qquad (7)$$

and

$$Y_j = \gamma_1 \exp(-k_1 t) - \gamma_2 \exp(-k_2 t) + Y_j^{\infty}, \qquad (8)$$

where k_1 and k_2 are rate constants, c_1^0 and c_2^0 are the concentrations at time $t = 0$, c_2^{∞} is the limiting concentration of bonds, and γ_1 and γ_2 are coefficients which are functions of c_1^0, c_2^0, and c_2^{∞}.

The plot of function (8) has an extremum and the corresponding asymptotic section. Thus for relatively simple hypotheses, the curves describing the variation of the characteristics of materials during ageing have a complex form. Nevertheless, in practical predictions of the changes in operating characteristics during thermal ageing, one normally employs elementary kinetic equations (of zero, first, and second orders), the treatment being limited in the case of complex $Y_j(t)$ curves to the description of their initial sections only[9-11,15]. There is a similar possibility of qualitative errors. This can be readily shown in relation to Eqn.(8). We shall assume that in the range of the temperatures of forced tests $k_1 > k_2$; the $Y_j(t)$ curves are then characterised by a minimum. The prediction based on the initial sections of these curves indicates a decrease of Y_j under real conditions. However, in consequence of the difference between the activation energies, there is also a possibility of a change in the ratio of the rates in the temperature range where the materials are used ($k_2 > k_1$). In this case there is a change also in the nature of the $Y_j(t)$ curve under real conditions (a maximum appears).

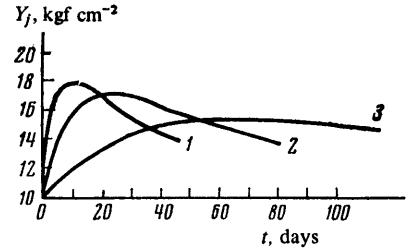


Figure 2. Calculated $Y_j(t)$ curves at different temperatures (°C): 1) 90; 2) 80; 3) 70.

We shall illustrate this by the following example. Suppose that the variation of the characteristic Y_j (for example, the short-term strength) is described by Eqn.(8) with $\gamma_1 = 13.8$, $\gamma_2 = 9.8$, $Y_j^{\infty} = 6$ kgf cm^{-2}, $k_1 = 7.4 \times 10^{-6} \exp(-14\,700/RT)$ days^{-1}, and $k_2 = 3.2 \times 10^{17} \exp(-30\,000/RT)$ days^{-1}. The calculated $Y_j(t)$ curves at 90°, 80°, and 70 °C have the form shown in Fig.2. The prediction based on the initial sections of these curves (up to the $Y_j = 12$ kgf cm^{-2} level), fitted by a first-order equation, indicates an increase of Y_j to 11.1 kgf cm^{-2} after ten years at 20 °C. On the other hand, calculation of the predicted $Y_j(t)$ curve by the initial Eqn.(8) indicates a decrease of the characteristic from 10.0 kgf cm^{-2} to 6.6 kgf cm^{-2} (Fig.3).

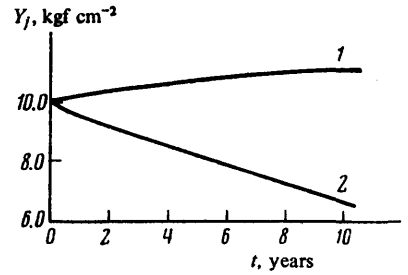


Figure 3. Predicted $Y_j(t)$ curves at 20 °C: 1) calculated from the initial sections of the curves in Fig.2; 2) calculated from the Eqn.(8).

Another common method of predicting the change in the properties of a polymeric material on thermal ageing is the so-called graphoanalytical method[10-14,21,22]. The essence of the method consists in the determination of the time t_{Y_j} for the attainment of identical values of Y_j from experimental

$Y_j(t)$ curves at different temperatures. The results are used to plot $\ln t_{Y_j} = f(1/T)$ and to find the time at the operating temperature by a linear extrapolation. The predicted $Y_j(t)$ curve at the operating temperature can be constructed on the basis of the complete set of values obtained.

It is easy to show that the linear relation between $\ln t_{Y_j}$ and $1/T$ is possible only in the case where the change in the characteristics is described by the kinetic equation

$$\frac{dY_j}{dt} = -A_0 \exp\left(-\frac{U}{RT}\right) f(Y_j). \qquad (9)$$

This postulates in its turn that the parameter U is independent of Y_j, i.e. that the $\ln t_{Y_j} = f(1/T)$ linear plots are parallel for different Y_j. This limits the region of applicability of the combined graphical and analytical method. The same limitation applies also to the familiar method of transformation coefficients[23]. In the case of curves with extrema, the application of these methods can also lead to qualitative errors in predicting the changes in the properties of materials.

It follows from the foregoing that, when the mechanism of ageing is unknown, in order to increase the reliability of the prediction of the changes in the properties of a polymeric material one must endeavour to discover the principal components of the process involving a change in Y_j and to obtain an analytical description of the latter. For this purpose, one can use the procedures of formal kinetics[23,24]. Frequently the form of the $Y_j(t)$ curves can be suggested by a version of the analytical curve fitting method. For example, in the case of S-shaped curves one can use formally the autocatalytic[23,24] or Kolmogorov–Erofeev[25,27] equation; experimental curves with asymptotic sections can be described by Eqn.(8). In the latter case, in particular, the parameters of the equation can be found by graphical or analytical methods[28,29] and Y_j^∞ is obtained by extrapolating the linearised relation $dY_j/dt = f(Y_j)$, corresponding to the last section of the $Y_j(t)$ curve, to the zero value of dY_j/dt or by the method# quoted by Shenk[30].

Naturally, mathematical modelling methods can be used for prediction on the basis of $Y_j(t)$ curves when the ageing mechanism is unknown[31].

We shall indicate yet another method whereby experimental $Y_j(t)$ curves can be fitted. Applying the methods for the expansion of functions, it is easy to show that Eqn.(6), corresponding to different varieties of relation (5), leads to a possible representation of the function $Y_j(t)$ by the experimental series

$$Y_j = Y_j^\infty + \sum_{i=1}^{n} \gamma_i \exp(-k_i t), \qquad (10)$$

where γ_i can be both positive and negative. The coefficients of Eqn.(10) naturally cannot always have a clear-cut physical significance, but, by fitting this equation to experimental data, one increases significantly the accuracy of the prediction and the determination of the principal components of the process involving the variation of $Y_j(t)$ is to some extent guaranteed. The coefficients of Eqn.(10) can be determined by the above procedure for Eqn.(8). Here the procedure used to search for the coefficients of the equation can reveal the fundamental stages (components) of the process involving the variation of $Y_j(t)$.

The method is based on the solution of the $Y_j = f(t)$ relation linearised with respect to t.

As an example, we shall consider the ageing of rubber based on SKMS-10 raw rubber. Fig.4 presents data for the accumulation of the residual deformation (ε_{res}) of the rubber under natural conditions. Analysis shows that the experimental data for the ageing of this rubber at 50–90 °C[32] are described satisfactorily by the equation

$$\varepsilon_{res} = \varepsilon_{res}^\infty - \gamma_1 \exp(-k_1 t) - \gamma_2 \exp(-k_2 t), \qquad (11)$$

where $\varepsilon_{res}^\infty = 97.5\%$, $\gamma_1 = 68.5\%$, $\gamma_2 = 29.0\%$, $k_1 = 3.2 \times 10^8 \exp(-16\,300/RT)$ days^{-1}, and $k_2 = 2.5 \times 10^{10} \exp(-17\,400/RT)$ days^{-1}. The $\varepsilon_{res}(t)$ for the regions of Central Asia and Transbaikal were calculated from the relations obtained. Fig.4 shows that the prediction is confirmed satisfactorily by observations carried out over many years.

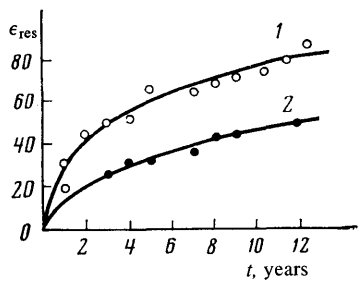


Figure 4. Kinetics of the accumulation of the residual deformation in rubber on storage in the regions of Central Asia (curve *1*) and Transbaikal (curve *2*) [the calculated curves were plotted on the basis of Eqn.(11) for $T_0 = 295.5$ K (curve *1*) and 283 K (curve *2*); the experimental points are based on the data of Dobrosklonskaya et al.[32]].

Mechanical stresses can have a significant influence on the rates of chemical reactions[33]. Under the influence of mechanical loads, chemical bonds are ruptured in polymers and free radicals are formed, giving rise to a chain of subsequent reactions[34]. The accelerating effect of mechanical stresses on thermal degradation processes in low-pressure polyethylene has been studied experimentally[35]. It has been shown[36] that mechanical stresses influence the apparent activation energy and the pre-exponential factor for the ageing of rubbers. According to the theory of absolute reaction rates[33], this implies that the stresses influence not only the energy barrier for the reactions but also the entropy of activation, which reflects the necessity for a specific orientation of the macromolecules.

Since the activation energy depends on the extent of the stresses, it is useful to study the ageing of materials in the stressed state at different temperatures under the conditions of constant stresses. The rates of processes then obey the Arrhenius equation, which can be used for extrapolation in the prediction. Tests under conditions of constant deformation complicate the task involved in the prediction owing to the temperature dependence of the rate of relaxation of stresses. Because of this, the level of stresses is different at different temperatures and hence there is a change in the apparent activation energy for the process. The use of the simple Arrhenius equation for prediction is in this case illegitimate.

The establishment of exact quantitative relations between the rate of ageing, on the one hand, and temperature and the extent of the stress on the other, makes it possible to calculate by numerical integration methods the predicted changes in the characteristics of materials under conditions of non-stationary stresses and temperatures[36].

IV. CHANGES IN THE PROPERTIES OF MATERIALS DUE TO MASS TRANSFER PROCESSES

Mass transfer phenomena are due to contact between the polymeric material and the surrounding medium and with other elements of the given articles. There is then a possibility of both physical and chemical transformations. Physical transformations are due to plasticisation, swelling, the formation of pores, etc.; chemical transformations are caused by the interaction of the diffusing substance with different functional groups of the polymer.

In the study of the interaction of a given article with the environment one usually investigates the changes of characteristics as a function of the duration of the influence of the medium (for example, increase in moisture content)[16-18]. The results of such tests indicate a sensitivity of articles to particular influences, but they are insufficient for the solution of the problems of prediction, since they refer to a specific geometry of the specimen, degree of penetration, etc.

For predictions of the changes due to physical transformations, it is necessary to establish the law governing the variation of the concentration of the diffusing substance with time at any point within the article:

$$a_i = a_i(r, t) \tag{12}$$

(here a_i is the concentration and r the flux coordinate) and the dependence of the characteristic of the material on concentration:

$$Y_j = Y_j(a_i). \tag{13}$$

By solving the mass transfer equation[29]

$$\frac{\partial \mu}{\partial t} = D\nabla^2\mu, \tag{14}$$

where μ is the chemical potential and D the diffusion coefficient, one determines the law governing the variation of concentration $a_i(r, t)$. The dependence of the characteristics of the material on the concentration $Y_j(a_i)$ is established experimentally. Simultaneous solution of Eqns.(12) and (13) yield the relation

$$Y_j = f(r, t). \tag{15}$$

If the diffusing substance participates in the chemical reactions responsible for the changes in the properties of the material) for example, water in hydrolytic degradation reactions[37-41]), then in the prediction one must solve the non-stationary kinetic problem taking into account the diffusion of the reactants:

$$\frac{\partial \mu}{\partial t} = D\nabla^2\mu - g(\mu), \tag{16}$$

where $g(\mu)$ is the rate of loss of the diffusing reactant (in units of chemical potential) owing to the chemical reaction. An evident condition for the solution of the problem is the determination of the mechanism and kinetics of the chemical reaction involving the diffusing reactant, which determine the $g(\mu)$ relation and the $Y_j = f(c_1, c_2, \ldots, c_n, a_i)$ relations.

The problem of the influence of atmospheric moisture is particularly important. It is known that, for many constructional polymeric materials, a change in humidity by several hundredths per cent leads to significant changes in operating properties. The endeavour to take into account the influence of moisture in accelerated tests for ageing (the so-called thermal-humidity ageing) is frequently expressed by the fact that tests at elevated temperatures are carried out at the level of the real relative humidity[42-44] (for example, 80 °C and a humidity of 80%). While the humidity under storage conditions is apparently reproduced, such tests can lead to considerable errors since the limiting (equilibrium) moisture content of the material changes significantly as the temperature is altered. This leads to non-equivalent changes in the properties of the material for purely physical reasons.

In order to separate chemical and physical transformations in thermal-humidity ageing, one can employ the method of conditioning the specimens, which consists in the fact that before and during thermal-humidity tests the specimens are maintained at the same relative humidity and temperature until the attainment of a state of equilibrium before measuring the characteristics. The conditioning method is based on the reversibility of the changes in the properties of the material due to physical transformations. The changes in properties detected in the course of tests on the material are due solely to chemical transformations.

The tests involved in estimating the changes in the properties of materials due to physical transformations are carried out by maintaining the specimens at different humidities at a low temperature (20–25 °C). Under these conditions, chemical transformations are hardly manifested during the experiment. The experiments are used to determine the sorption isotherms, the diffusion coefficients, and the $Y_j(a_i)$ relation.

We shall consider the changes in the operating properties of polymeric materials due to chemical transformations in thermal-humidity ageing. The simplest example is the case where the characteristic of the material Y_j investigated is determined by a single type of bond subject to hydrolytic degradation. Assuming that

$$Y_j = \alpha c^n, \ \frac{dc}{dt} = -k_1 cW, \ \frac{dW}{dt} = -k_1 cW + k_2(W_e - W), \tag{17}$$

where W and W_e are the current and limiting (equilibrium) moisture contents of the material and k_2 is the mass exchange rate constant, we obtain for the quasi-stationary state ($dW/dt \cong 0$) [45]

$$W = \frac{k_2 W_e}{k_1 c + k_2}, \ \frac{dc}{dt} = -\frac{k_1 c k_2 W_e}{k_1 c + k_2}. \tag{18}$$

When the process takes place in the kinetic region (for example, in the case of film materials), we have

$$k_2 \gg k_1 c, \ \frac{dc}{dt} = -k_1 W_e c; \ \frac{dY_j}{dt} = -\tilde{k}_1 Y_j; \ \tilde{k}_1 = nk_1 W_e. \tag{19}$$

In the diffusion region

$$k_2 \ll k_1 c, \ \frac{dc}{dt} = -k_2 W_e; \ \frac{dY_j}{dt} = -\tilde{k}_2 Y_j^{1-1/n}, \ \tilde{k}_2 = n\alpha^{1/n} k_2 W_e. \tag{20}$$

Using the equation of the Freundlich isotherm

$$W_e = \chi p^{1/\nu}, \tag{21}$$

the Clausius–Clapeyron equation for equilibrium systems

$$\frac{d \ln p}{d(1/T)} = -\frac{Q}{R} \tag{22}$$

(p is the water vapour pressure, Q the heat of sorption, and χ and ν are coefficients), and the equation for the temperature dependence of the constants k_1 and k_2, it is easy to show that

$$\tilde{k}_1 = a_1 p^{1/\nu} \exp\left(-\frac{U - Q/\nu}{RT}\right); \ \tilde{k}_2 = a_2 p^{1/\nu} \exp\left(-\frac{E - Q/\nu}{RT}\right), \tag{23}$$

where U and E are respectively the apparent activation energy for the reaction and diffusion and a_1 and a_2 are coefficients.

Eqns.(23) determine the temperature dependence of the effective rate constants $\tilde{k}_1$ and $\tilde{k}_2$ for the variation of the characteristic Y_j. If tests at different temperatures are carried out at $p = \text{const.}$, then it follows from Eqn.(23) that the dependences of $\ln \tilde{k}_1$ and $\ln \tilde{k}_2$ on $1/T$ are linear, which makes it possible to employ them for the prediction of the rate of change of Y_j when the material is stored under real conditions. The apparent activation energy is then determined by the differences $U - Q/\nu$ and $E - Q/\nu$ respectively.

If the materials are tested at a constant relative humidity of air ϕ, then, bearing in mind that

$$p = p_{sat} \cdot \varphi; \quad p_{sat} = \lambda \exp(-L/RT) \tag{24}$$

(p_{sat} is the water vapour pressure, L the heat of vaporisation, and λ a coefficient), we obtain

$$\tilde{k}_1 = b_1 \varphi^{1/\nu} \exp\left(-\frac{U - Q/\nu + L/\nu}{RT}\right); \quad \tilde{k}_2 = b_2 \varphi^{1/\nu} \exp\left(-\frac{E - Q/\nu + L/\nu}{RT}\right), \tag{25}$$

where b_1 and b_2 are coefficients. Eqns.(25) also make it possible to use for prediction the linear dependences of $\ln \tilde{k}_1$ and $\ln \tilde{k}_2$ on $1/T$, but naturally with coefficients different to those in Eqn.(23).

The above relations (17)–(25) describe the changes in characteristics occurring in consequence of chemical transformations under the influence of water. The corresponding coefficients can be found from experimental $Y_j(t)$ curves obtained by the method of conditioning the specimens. The overall change in the properties of the material is determined as the sum of the changes due to chemical and physical transformations.

One must note that Eqns.(17)–(25) refer to certain limiting situations. In the general case a correct prediction of the changes in the properties of the material is possible on the basis of the diffusion-kinetic model defined by Eqn.(16).

V. PREDICTION OF THE LIFETIMES OF MATERIALS

Ideas concerning the breakdown of materials as a process occurring in time have come to be generally accepted[47–53]. The breakdown of bodies under the influence of stresses can be regarded as a chemical degradation reaction activated by the stress. Different types of reactions have been analysed in a number of studies[54–58] and in the review of Deyun et al.§

The time before the breakdown of the material under the influence of a constant stress σ under the conditions of a constant temperature is referred to as the lifetime of the material τ. Experimental $\tau(\sigma)$ relations constitute the basis for the prediction of the lifetime. The empirical relations (at $T = \text{const.}$)

$$\tau = A \exp(-\alpha\sigma), \tag{26}$$

$$\tau = B\sigma^{-m}, \tag{27}$$

where α, m, A, and B are coefficients, have come to be most widely used.

Eqn.(26) usually holds for rigid polymeric materials, while Eqn.(27) is valid for elastomers. It has been shown[55,60] that Eqns.(26) and (27) constitute limiting cases of more general $\tau(\sigma)$ relations; the region of their applicability is determined by the extent of the stresses. Eqn.(27) holds as a rule in the region of low stresses and Eqn.(26) in the region of higher stresses. Since in experiments involving the determination of the $\tau(\sigma)$ relation one measures the time before the breakdown of the specimen under the influence of the stress, τ is frequently referred to as the mechanical lifetime.

During storage and use, articles made from polymeric materials are subjected to stresses and temperatures which vary with time. Under these conditions, the lifetime can be calculated on the basis of particular models of the process (physical, chemical, and mechanical)[48,49,55–58,60,61].

The breakdown of the material is characterised by the degree of accumulation of defects. From the standpoint of chemical kinetics, the degree of accumulation of defects in the material is measured by the ratio of the amount of ruptured bonds to the total number of bonds per unit cross-sectional area of the specimen. In the mechanics of continuous media, the ratio of the time of application of the load to the lifetime or ratio of the acting stress to the breaking stress as well as other criteria serve as measures of the extent of damage at a constant acting stress, while under non-stationary conditions the corresponding integral functions serve as the relevant measures. The limiting degree of accumulation of defects, usually set equal to unity, serves as a criterion of the breakdown.

The criteria of Bailey[48,49]

$$\int_0^{t_b} \frac{dt}{\tau(\sigma, T)} = 1, \tag{28}$$

Il'yushin[60]

$$\int_0^{t_b} \frac{d\sigma}{S(t_b - t)} = 1 \tag{29}$$

and others[61,62] have come to be most widely used in engineering practice [in these relations t is the time of application of the load, t_b the time before breakdown, and S the breaking (constant) stress]. Being of phenomenological origin, these criteria have a physical basis in many instances. For example, the applicability of Bailey's criterion has been examined from the standpoint of the kinetics of the development of cracks[63].

Much experience has been gained in engineering practice as regards these criteria and the limitis of their applicability have been established. Bailey's criterion, defined by Eqn. (28), which expresses the principle of the summation of defects but does not take into account the history of the applied load, is the simplest.

In contrast to Bailey's criterion, Il'yushin's criterion, defined by Eqn.(29), reflects the history of the applied load, while non-linear criteria examined in a number of studies[60–62] make it possible to take into account more accurately the complex laws governing the effect of the load and the mechanical behaviour of bodies in terms of empirical coefficients.

As already stated, the breakdown criteria are used to estimate the lifetime of the material (article) under the conditions of a non-stationary stress. The properties of the material are then assumed to be unchanged. Under real storage and operating conditions, the properties of the polymeric material vary owing to ageing, mass transfer, etc. processes. The real lifetime of the material can then differ significantly from the lifetime predicted on the basis of the results of mechanical tests in which the effect of factors other than stresses is usually excluded[63].

§ See E.V.Deyun, G.B.Manelis, E.V.Polianchuk, and I.P.Smirnov, Uspekhi Khim., **49**, 1574 (1980) [Russ.Chem. Rev., No.8 (1980)].

The criteria of long-term strength, extended to the case of physicochemical transformations, will be used to predict the real lifetime. As a simple example, we shall examine Bailey's criterion, which can be formulated as follows in this instance:

$$\int_0^{t_b} \frac{dt}{\tau(\sigma, T, \eta)} = 1, \tag{30}$$

where η is the extent of the change in the properties of the material owing to physicochemical transformations. Assuming, in accordance with Eqn.(27), that

$$\tau = B(\eta)\sigma^{-m(\eta)} \tag{31}$$

and taking into account the fact that $\eta = \eta(t)$, we obtain from Eqn.(30) for σ, $T = \text{const.}$,

$$\int_0^{\tau_s} B^{-1}(t)\,\sigma^{m(t)}\,dt = 1, \tag{32}$$

where τ_S is the time before the breakdown of the material for constant stresses and at a constant temperature (the lifetime). Having established the characteristics of the variation of $B(t)$ and $m(t)$ during ageing, mass exchange, and other transformations, it is possible to calculate the lifetime from Eqn.(32). In the general case calculations by Eqn.(30) or (32) are performed by numerical integration.

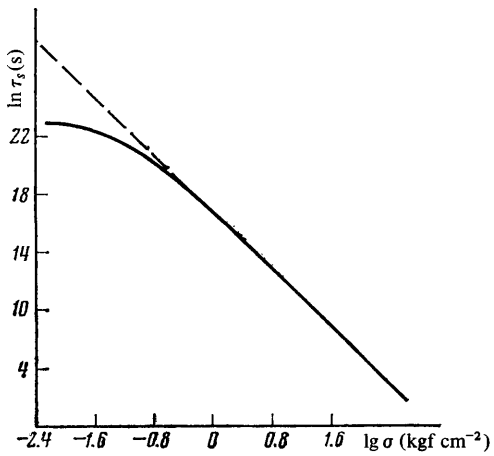


Figure 5. Dependence of $\ln \tau_S$ on $\ln \sigma$ for $B_0 = 10^7$ s, $m = 5$, and $k = 5.7 \times 10^{-9}$ s^{-1} (the curve in the absence of transformations is shown dashed)[64].

In order to elucidate the fundamental characteristics of the $\tau_S(t)$ relation, we shall consider the following example. It is known that, in the ageing of many polymeric materials up to a degree of conversion of 25–50%, the exponent m in Eqn.(27) hardly changes; the variation of the lifetime is due to the variation of the coefficient B. Assuming that the coefficient B changes as a result of ageing in accordance with the first-order equation

$$B = B_0 \exp(-kt), \tag{33}$$

where k is the rate constant for the ageing process, we obtain, after integrating Eqn.(32),

$$\tau_s = k^{-1} \cdot \ln(1 + kB_0\sigma^{-m}) = k^{-1} \ln(1 + k\tau_0), \tag{34}$$

where $\tau_0 = B_0\sigma^{-m}$ is the lifetime determined by the action of mechanical stresses. For $k\tau_0(\sigma) \ll 1$, we have

$$\ln(1 + k\tau_0) \simeq k\tau_0;\ \tau_s \simeq \tau_0. \tag{35}$$

This condition limits the region where Eqns.(26) and (27) can be used to predict the strength and lifetime of the materials. When $k\tau_0 \gg 1$, we have $\tau_S < \tau_0$, i.e. the real lifetime is shorter than the mechanical lifetime.

Evidently, when $\sigma \gg (kB_0)^{1/m}$, we have

$$\ln \tau_s = \ln B_0 - m \ln \sigma, \tag{36}$$

and, when $\sigma \ll (kB_0)^{1/m}$, we have

$$\tau_s = k^{-1} \ln(kB_0) - mk^{-1} \ln \sigma\ . \tag{37}$$

Thus the linear relation $\ln \tau_S = f(\ln \sigma)$ is converted into the linear relation $\tau_S = f(\ln \sigma)$. The lifetime curve constructed by plotting $\ln \tau_S$ against $\ln \sigma$ shows a characteristic inflection (Fig.5). Fig.5 shows that the difference between the lifetimes τ_S and τ_0 for low stresses can reach two decadic orders of magnitude.

This approach to the prediction of the lifetime of a polymeric material under the conditions of physicochemical transformations can be used virtually whatever the law governing the variation of the parameters of the mechanical lifetime and whatever other criteria of long-term strength are employed. A necessary condition for this purpose is the study of the kinetics of the physicochemical transformations and the determination of the relation between the parameters of the mechanical lifetime and the degree of transformation.

VI. ACCELERATED TESTS ON ARTICLES MADE FROM POLYMERIC MATERIALS

Articles made from polymeric materials differ from specimens of the materials in the first place by the presence of stresses due to the geometry and size of the articles and also the external influences to which they are subjected. In order to estimate the lifetime of articles made from polymeric materials, accelerated tests are frequently resorted to, i.e. tests are made on the whole article or on its individual components for the influence of various operating factors (temperature and humidity of the surrounding air, temperature differences, radiation, and applied loads).

Accelerated tests on an article without a detailed elucidation of the characteristic features of the variation of the properties of the relevant materials are frequently regarded as the only method of predicting their lifetime. The task to be performed in selecting the conditions for such tests is believed to involve the modelling of the operating conditions[65]. This approach can hardly be regarded as useful, since a well-founded choice of conditions for the tests is impossible without knowing the characteristics of the variation of the properties of the materials. Furthermore, there is a possibility of the case where the predicted changes in the characteristics of the article under storage and operating conditions can amount to a fraction per cent and complex and expensive tests are then pointless.

We believe that the task of accelerated tests is not the modelling of external factors but the reproduction of the changes in the characteristics of the articles which are to be expected during storage and use. These tests are carried out in order to confirm the predicted changes in the characteristics of the articles under the influence of various factors only in those cases where the predicted changes are significant and have a negative influence on the suitability of the material for its purpose and when allowance for the changes in all the characteristics of the article is difficult. The conditions of accelerated tests on articles can be chosen only on

the basis of the study of the kinetics of the variation of the characteristics of the materials. The parameters of the tests are selected on the basis of the condition that identical changes in the operating properties of the polymeric material under operating conditions are reproduced in the accelerated tests:

$$\Delta Y_j(t_0, \chi_0) = \Delta Y_j(t_a, \chi_a). \quad (38)$$

where t_0 and t_a are the storage time and the duration of accelerated tests and χ_0 and χ_a are the parameters of the storage conditions and the conditions of the accelerated tests (temperature, stress, relative humidity, radiation dose, etc.). Tests designed to reproduce the changes in the properties of the material during ageing, mass transfer, and under the influence of stresses are special cases.

Tests for thermal ageing are carried out by maintaining the article at a specified constant temperature T_a during the so-called equivalent time t_a. In simple cases where the change in Y_j is described by Eqn.(9), the time t_a can be calculated from the relation[65,66]

$$t_a = t_0 \exp\left[\frac{U}{R}\left(\frac{1}{T_a} - \frac{1}{T_0}\right)\right]. \quad (39)$$

Calculation of the equivalent time t_a by Eqn.(39) without taking into account the specific kinetic features of $Y_j(t)$ can lead to significant errors. The most general method for the determination of t_a therefore consists of the following steps. On the basis of the known kinetics of the variation of the characteristic of the material during ageing, one plots the predicted curve $Y_j(t)$ for specified storage conditions ($T = T_0$) and the curve $Y_j(t)$ under forced conditions ($T = T_a$). The greatest changes in Y_j are determined from the predicted curve and the time t_a corresponding to the attainment of these changes at $T = T_a$ is found (Fig.6). One must then bear in mind that in the case of complex processes the maximum changes in properties cannot always be reproduced in accelerated tests. Thus, for processes described by Eqn.(8), there exists a temperature T_* above which no changes occurring under real storage conditions can be reproduced owing to the inversion of the curves $Y_j(t)$. This is in no way caused by a change in the mechanism of the processes but is due to a change in the ratio of their rate constants. The quantity T_* is defined by the expression

$$T_* = \frac{U_1 - U_2}{R \ln (A_1/A_2)}, \quad (40)$$

where U_1 and U_2 are apparent activation energies and A_1 and A_2 are the pre-exponential factors associated with the corresponding rate constants. One should bear in mind that, when $T < T_*$, it is possible to reproduce only those changes which do not exceed the level corresponding to T_a.

In accelerated tests on articles made from different polymeric materials the problem of the simulation of several processes arises. The choice of the equivalent times t_a on the basis of the apparent activation energy for a certain process in any given material can lead to unduly extensive or, conversely, insufficient transformations in other materials. Analysis shows that the problem of the reproduction of the real changes in Y_j in a multielement article can be solved rigorously only in a few instances. These include cases where Eqn.(9) holds for each element (material) and there is a definite relation between the kinetic parameters[66].

The parameters of the conditions of accelerated tests for the influence of mass transfer processes can also be chosen from the condition for the attainment of identical changes in properties during storage and accelerated tests. For this purpose, one calculates from the solution of mass transfer equations the change in the concentration of the diffusing substance under storage conditions and in accelerated tests: $a_i = f(t, r)$. Using the relation $Y_j = f(a_i)$, one plots on the basis of the data obtained the curves $Y_j = f(t, r)$ from which one determines the duration of the tests in accordance with the scheme illustrated in Fig.6. In this case accelerated tests are carried out at an elevated temperature and concentration of the diffusing substance (for example, atmospheric moisture). These tests can be combined with tests of the reproducibility of the changes in the properties of the material during ageing.

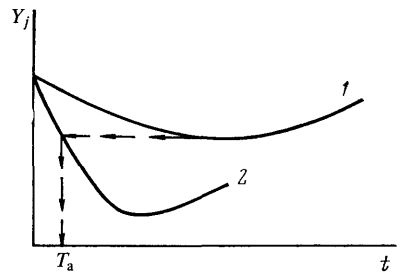


Figure 6. Selection of the duration of tests: 1) predicted $Y_j(t)$ curve describing the variation of the characteristics of the material under the conditions of storage or use at $T = T_0$; 2) the curve describing the variation of the characteristics of the material under the conditions of accelerated tests at $T = T_a$.

Under the storage conditions, articles made from polymeric materials are subjected to prolonged stresses. These include stresses due to gravitational forces, stationary and non-stationary temperature stresses induced by seasonal and diurnal changes in temperature, etc. Well-founded conditions for accelerated tests, designed to check the influence of various forces (the level of stresses, amplitude, temperature, duration), are selected on the basis of identity conditions in the accumulation of defects during storage and accelerated tests[66]:

$$\pi(T_0, \sigma_0^e, \eta_0, t_0) = \pi(T_a, \sigma_a^e, \eta_a, t_a), \quad (41)$$

where π is the level of accumulated defects and σ^e are equivalent stresses in the article. When Bailey's integral is used as a measure of the accumulation of defects (π), the above condition is formulated as follows:

$$\int_0^{t_0} \frac{dt}{\tau(\sigma_0^e, T_0, \eta_0)} = \int_0^{t_a} \frac{dt}{\tau(\sigma_a^e, T_a, \eta_a)}. \quad (42)$$

Consider the following example. We assume that the article made from a polymeric material is stored at a temperature T_0 and is subjected to a stress σ_0^e during a period t_0. The corresponding quantities σ_a^e and T_a are chosen for the accelerated tests. Assuming for simplicity that $\eta_0 = \eta_a = 0$, we obtain from Eqn.(42)

$$t_a = t_0 \frac{\tau(\sigma_a^e, T_a)}{\tau(\sigma_0^e, T_0)}. \quad (43)$$

In this case, when the relation $\tau(\sigma)$ is determined by Eqn. (27), we have, for $T_a = T_0$,

$$t_a = t_0 \left(\frac{\sigma_0^e}{\sigma_a^e}\right)^m. \quad (44)$$

Since for a polymeric material we usually have $m > 6$, the increase of stresses under the conditions of accelerated tests makes it possible to reduce greatly their duration. For example, for $\sigma_a^e = 2\sigma_0^e$ and $m = 7$, we obtain $t_a < 0.01 t_0$ when $T_a = T_0$.

For an exponential relation between the lifetime and σ [Eqn. (26)], it follows from Eqn.(43) that

$$t_a = t_0 \exp [\alpha (\sigma_0^e - \sigma_a^e)]. \quad (45)$$

When $\sigma = \text{const.}$, the following relation usually holds[48,49]:

$$\tau = p \exp (U_b/RT) \quad (46)$$

where U_b is the apparent activation energy for the breakdown and p a coefficient. It follows from Eqns.(43) and (46) that, when $\sigma_a^e = \sigma_0^e$,

$$t_a = t_0 \exp \left[\frac{U_b}{R} \left(\frac{1}{T_a} - \frac{1}{T_0} \right) \right]. \quad (47)$$

The above relations indicate the possibility of intensifying accelerated tests on articles by the application of forces and elevated temperatures.

This approach can be used also in tests for cyclic influences of forces[66]. From Eqn.(41), one can calculate the time during which articles must be thermostatted at negative temperatures and the number of cycles simulating the influence of diurnal oscillations in temperature.

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It follows from the foregoing that the endeavour to simplify unduly the methods for the interpretation of kinetic curves and the determination of the parameters of accelerated tests can lead to gross errors, including qualitative errors.

A correct prediction is based on the study of the kinetics of the variation of the properties of materials under the influence of various factors and the mechanisms of the processes taking place.

REFERENCES

1. GOST 16 350-70. Klimat SSSR. Raionirovanie i Kharakteristiki Klimaticheskikh Parametrov dlya Promyshlennykh Izdelii" [GOST (USSR Government Standard) 16 350-70. The Climate of the USSR. Regional Variation and Characteristics of the Climatic Parameters for Industrial Articles].
2. V.E.Zotkin and V.N.Vorob'ev, Standarty i Kachestvo, No.8, 52 (1978).
3. V.D.Goikhman, A.D.Moshchenskii, and L.V.Selezneva, Kauchuk i Rezina, No.4, 49 (1968).
4. B.D.Goikhman and T.P.Smekhunova, Fiziko-Khimicheskaya Mekhanika Materialov, No.1, 92 (1977).
5. L.S.Fel'dshtein, M.G.Muradova, and L.G.Angert, Kauchuk i Rezina, No.6, 26 (1974).
6. A.G.Dement'ev, O.G.Tarakanov, P.I.Seliverstov, and E.V.Belova, Plast.Massy, No.5, 47 (1974).
7. A.K.Zhitinkina, A.G.Dement'ev, N.A.Tolstykh, and O.G.Tarakanov, Plast.Massy, No.5, 50 (1974).
8. A.G.Dement'ev, O.G.Tarakanov, P.I.Seliverstov, and E.V.Belova, Plast.Massy, No.5, 52 (1974).
9. I.F.Legrei and M.N.Bokshitskii, Plast.Massy, No.2, 54 (1974).
10. E.I.Kirillova, Plast.Massy, No.3, 49 (1973).
11. N.P.Lazareva, S.S.Khin'kis, M.F.Utyugov, M.S.Borodulina, T.S.Sokolova, and E.P.Matveeva, Plast.Massy, No.7, 75 (1973).
12. N.N.Pavlov, V.A.Sade, and G.A.Kudryavtseva, Plast. Massy, No.3, 52 (1974).
13. E.L.Vinogradov, L.I.Godunova, A.M.Lobanov, N.V.Lysenko, L.M.Terent'ev, and S.S.Khin'kis, Plast. Massy, No.4, 44 (1976).
14. A.G.Dement'ev, L.N.Malinin, V.V.Strakhov, and V.K.Anan'ev, Plast.Massy, No.1, 52 (1977).
15. E.L.Vinogradova, M.G.Bruk, and A.L.Vdovina, Plast. Massy, No.5, 51 (1977).
16. M.E.Sarkisyan, V.L.Kravchenok, and V.S.Petrov, Mekhanika Kompozitnykh Materialov, **1**, 163 (1979).
17. V.M.Shcherbakov, S.V.Mazur, Kh.V.Solomon, and V.M.Gal'perina, Plast.Massy, No.10, 37 (1962).
18. G.O.Tatevos'yan and I.G.Kuznetsova, Plast.Massy, No.2, 52 (1963).
19. A.V.Tobolsky, "Properties and Structures of Polymers" (Translated into Russian), Izd.Khimiya, Moscow, 1964.
20. B.A.Dogadkin, B.K.Karmin, and I.I.Gol'berg, Dokl. Akad.Nauk SSSR, **53**, 331 (1946).
21. GOST 9033-74. Reziny. Metod Prognozirovaniya Izmeneniya Svoistv pri Termicheskom Starenii" [GOST (USSR Government Standard) 9033-74. Rubbers. Methods for the Prediction of the Changes in Properties on Thermal Ageing].
22. GOST 9035-74. Reziny. Metod Uskorennogo Opredeleniya Garantiinogo Sroka Khraneniya Uplotnitel'nykh Detalei Nepodvizhnykh Soedinenii [GOST (USSR Goverment Standard) 9035-74. Rubbers. Method for the Rapid Determination of the Guaranteed Storage Time of the Sealing Components of Fixed Junctions].
23. N.M.Emanuel' and D.G.Knorre, "Kurs Khimicheskoi Kinetiki" (A Course of Chemical Kinetics), Izd. Vysshaya Shkola, Moscow, 1969.
24. S.W.Benson, "The Foundations of Chemical Kinetics" (Translated into Russian), Izd.Mir, Moscow, 1964.
25. A.N.Kolmogorov, Izv.Akad.Nauk SSSR, Ser.Mat., 3, 355 (1937).
26. B.V.Erofeev, Dokl.Akad.Nauk SSSR, **52**, 515 (1946).
27. D.A.Young, "Decomposition of Solids" (Translated into Russian), Izd.Mir, Moscow, 1969.
28. A.A.Tatarnikov, Kauchuk i Rezina, No.3, 34 (1976).
29. A.V.Lykov, "Teoriya Teploprovodnosti" (Theory of Thermal Conductivity), Izd.Vysshaya Shkola, Moscow, 1967.
30. N.E.Shenk, Int.J.Chem.Kinet., **6**, 577 (1973).
31. L.S.Polak (Editor), "Primenenie Vychislitel'noi Matematiki v Khimicheskoi i Fizicheskoi Kinetike" (Application of Computational Mathematics to Chemical and Physical Kinetics), Izd.Nauka, Moscow, 1969.
32. M.S.Dobrosklonskaya, V.G.Rebizova, and A.S.Kosenkova, Kauchuk i Rezina, No.4, 9 (1968).
33. S.Glasstone, K.J.Laidler, and H.Eyring, "Theory of Rate Processes" (Translated into Russian), Inostr. Lit., Moscow, 1948.
34. S.E.Bresler, S.N.Zhurkov, E.N.Kazbekov, E.M.Sominskii, and E.E.Tomashevskii, Zhur.Tekh.Fiz., **29**, 358 (1959).
35. V.E.Korsukov, V.I.Vettegren', I.I.Novak, and L.P.Zaitseva, Vysokomol.Soed., **16**, 1538 (1974).
36. G.I.Sarser, B.D.Goikhman, N.G.Kalinin, and A.N.Tynnyi, Fiziko-Khimicheskaya Mekhanika Materialov, No.1, 89 (1975).
37. N.Grassie, "Chemistry of High Polymer Degradation Processes" (Translated into Russian), Inostr.Lit., Moscow, 1959.
38. G.E.Zaikov and Yu.V.Moiseev, Plast.Massy, No.11, 43 (1972).
39. L.V.Ivanov, Yu.V.Moiseev, and G.E.Zaikov, Vysokomol.Soed., **14A**, 1057 (1972).

40. L.V.Ivanov, Yu.V.Moiseev, and G.E.Zaikov, Izv.Akad. Nauk SSSR, Ser.Khim., 2501 (1970).
41. G.E.Zaikov, Uspekhi Khim., **44**, 1805 (1975) [Russ. Chem.Rev., No.10 (1975)].
42. GOST 21 126-75. Izdeliya Elektrotekhnicheskie. Materialy, Pokrytiya, Uzly i Detali. Metody Uskorennykh Ispytanii na Dolgovechnost' i Sokhranyaemost' v Agressivnykh Sredakh. Obshchie Polozheniya [GOST (USSR Government Standard) 21 126-75. Electrotechnical Articles. Materials, Coatings, Junctions, and Components. Methods for Accelerated Tests for the Lifetime and Capacity for Storage in Corrosive Media. General Postulates].
43. GOST 9044-75. Pokrytiya Lakokrasochnye. Uskorennye Metody Opredeleniya Svetostoikosti [GOST (USSR Government Standard) 9044-75. Paint and Varnish Coatings. Accelerated Methods for the Determination of Resistance to Light].
44. GOST 17 171-71. Plastmassy. Metody Ispytaniya na Starenie pod Vozdeistviem Iskusstvennykh Klimaticheskikh Faktorov [GOST (USSR Government Standard) 17 171-71. Plastics. Methods for Tests for Ageing under the Influence of Artificial Climatic Factors].
45. D.A.Frank-Kamenetskii, "Diffuziya i Teploperedacha v Khimicheskoi Kinetike" (Diffusion and Heat Transfer in Chemical Kinetics), Izd.Nauka, Moscow, 1967.
46. S.Brunauer, "The Adsorption of Gases and Vapours" (Translated into Russian), Inostr.Lit., Moscow, 1948, Vol.1.
47. S.N.Zhurkov, Izv.Akad.Nauk SSSR, Neorg.Materialy, **3**, 1767 (1967).
48. V.R.Regel', A.I.Slutsker, and E.E.Tomashevskii, "Kineticheskaya Priroda Prochnosti Tverdykh Tel" (The Kinetic Nature of the Strength of Solids), Izd. Nauka, Moscow, 1974.
49. G.M.Bartenev and Yu.S.Zuev, "Prochnost' i Razrushenie Vysokoplastichnykh Materialov" (The Strength and Breakdown of Highly Plastic Materials), Izd.Khimiya, Moscow–Leningrad, 1964.
50. V.E.Gul', "Prochnost' Polimerov" (The Strength of Polymers), Izd.Khimiya, Moscow–Leningrad, 1964.
51. W.G.Knauss, Mekhanika (Periodicheskii Sbornik Perevodov Inostrannykh Statei), No.2, 116 (1974).
52. C.B.Henderson, P.H.Graham, and C.N.Robinson, Inst.Journ.of Fract.Mechan., **6**, 33 (1970).
53. A.S.Krausz and H.Eyring, "Deformation Kinetics", Wiley, Interscience, New York, 1975.
54. A.Tobolsky and H.Eyring, J.Chem.Phys., **11**, 125 (1943).
55. G.B.Manelis, L.P.Smirnov, and E.V.Polianchik, Dokl. Akad.Nauk SSSR, **215**, 1157 (1974).
56. G.B.Manelis, L.P.Smirnov, E.V.Polianchik, and S.N.Bloshenko, Vysokomol.Soed., **A19**, 86 (1977).
57. G.B.Manelis and E.V.Polianchik, Vysokomol.Soed., **A20**, 125 (1978).
58. G.B.Manelis, L.P.Smirnov, and E.V.Polianchik, Dokl. Akad.Nauk SSSR, **217**, 139 (1974).
59. B.D.Goikhman, Problemy Prochnosti, No.8, 18 (1972).
60. A.A.Il'yushin, Mekhanika Tverdogo Tela, No.3, 21.
61. V.V.Moskvitin, "Soprotivlenie Vyazkouprugikh Materialov" (The Resistance of Viscoelastic Materials), Izd.Nauka, Moscow, 1972.
62. Yu.Ya.Bart, V.P.Trifonov, A.B.Kozachenko, and N.I.Malinin, Mekhanika Polimerov, **5**, 791 (1975).
63. I.G.Barenblatt, V.M.Entov, and R.A.Salganik, Mekhanika Tverdogo Tela, No.2, 148 (1967).
64. B.D.Goikhman, Fiz.-Khim.Mekhanika Materialov, No.3, 65 (1975).
65. V.E.Zotkin, Standarty i Kachestvo, No.9, 62 (1977).
66. B.D.Goikhman, Plast.Massy, No.2, 56 (1971).