

Creep of Polycarbonate: Experiments and Correlation with Relaxation

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SYNOPSIS

The correctness and reliability of different methods of creep function calculations from relaxation curves were investigated by the computational experiment method. It was shown that an adequate description of some initial (relaxation) curve was not sufficient for the correct determination of the proper creep function. The best results can be achieved by the method of expansion of a relaxation curve into the discrete sum of exponents; some other procedures of analytical approximation of relaxation curves can lead to considerable unexpected errors in calculated creep functions.

The experiments were done with polycarbonate (PC) in the linear stress range and also at high stresses. The limits of linear viscoelastic behavior were determined.

INTRODUCTION

The application of polycarbonate (PC) as an engineering plastic requires the determination of a wide set of mechanical properties for this material. In particular, it is necessary to estimate its long-term behavior in creep and relaxation, as these kinds of deformation imitate those found for the most typical applications of different articles made from PC.

Direct creep measurements are not difficult in principle and can be made with homemade or serial devices. But in practice there are two points which must be considered. First, the problem of maintaining strictly constant stress should be solved. Second, such experiments are very prolonged and this leads to some methodological difficulties which influence the accuracy of measurements (for example: changes in temperature, humidity, and structure of a sample during the experiment; creep and relaxation of the sensor itself; and so on). For these reasons it would be attractive to use some theoretical (calculation) approaches to decrease the number of experiments needed to receive a reliable creep curve.

The potential for realizing this goal is contained in the linear theory of viscoelasticity which gives analytical expressions allowing calculation of the

creep function from a relaxation curve.¹ However, there are four questions which need to be answered:

1. Is the calculation of the creep function from a relaxation curve stable with respect to possible experimental errors?
2. What is the best way of approximation of the experimental relaxation curve in order to reach the best reliability of the final result?
3. What is the possible reliable time range in creep relating to the observed time scale of relaxation?
4. Where do the limits of linear behavior lie and what is the role of this factor?

This paper attempts to find general answers to the above questions and to illustrate them by computational simulation of the problem under discussion.

THEORY

This part of the paper will be devoted to the mathematical (computational) simulation of problems 1–4, formulated in the introduction. To do this one should choose definite analytical forms of viscoelastic functions and treat them as the “experimental” basis for further discussion.

As is well known, the relationship between relaxation modulus $G(t)$ and creep compliance $J(t)$ is expressed by an integral equation of the convolution type:^{1,2}

$$\int_0^t G(\tau)J(t-\tau) d\tau = t \quad (1)$$

and

$$G(t) = \phi(t) + G_\infty \quad (2)$$

$$J(t) = J_0 + \psi(t) + t/\eta \quad (3)$$

where $\phi(t)$ is the relaxation function, $\psi(t)$ is the creep function, G_∞ is the equilibrium elastic modulus, J_0 is the instantaneous compliance, and η is the viscosity.

To obtain the solution of Equation (1) one must invert a Laplace transform that is not always possible in the analytical form. That is the reason why concrete solutions of Equation (1) based on different analytical presentations of the relaxation and/or creep functions have been proposed and used by many authors.

One of the known exact solutions of Equation (1) will be taken as a reference curve. The mathematical (computational) experiment consists in comparing curves obtained by different approximation methods with the reference curve.

As the control (or reference) creep function a curve will be used that is determined by the following kernel:³

$$K(t) = \frac{e^{-\beta t}}{t} \sum \frac{[A\Gamma(\alpha)]^{\eta t \alpha \eta}}{\Gamma(\alpha \eta)} \quad (4)$$

The creep function is expressed by $K(t)$ as

$$\psi(t) = J_0 \int_0^t K(\tau) d\tau - t/\eta \quad (5)$$

The corresponding relaxation kernel has the form

$$R(t) = Ae^{-\beta t} t^{\alpha-1} \quad (0 < \alpha < 1) \quad (6)$$

and the relaxation function can be written as

$$\phi(t) = G_0 \left[1 - \int_0^t R(\tau) d\tau \right] - G_\infty \quad (7)$$

where G_0 is the instantaneous elastic modulus. It is important that the values of all these functions be calculated and tabulated for a wide range of parameters,³ so that knowing one of these (creep or relaxation) functions it is possible to find the other one with any desired accuracy. Let us consider this calculated relaxation curve as initial "experimental" datum. Then one can approximate it by different methods (the accuracy of measurements namely the maximum deviation in every point of the time scale being accepted to be equal to 10%) and calculate the creep function. The comparison of these newly calculated creep functions with the exact solution presented by Equations (4) and (5) will allow one to answer some questions concerning the correctness of the whole procedure, and in particular, the stability of the solution with respect to experimental errors when using different methods of approximation. This is the goal of the computational experiment.

In the text below the designation "experimental" will be omitted and the tabulated values of $\phi(t)$ and $\psi(t)$ which have been calculated will be used as the real experimental (or reference) pair of functions. In this case the dimension of time has no meaning as it can have any value.

Let us examine the possibility of approximating some experimental curve by the sum of exponential

Table I Approximation of the Relaxation Curve by the Sum of Exponents

Spectrum No.	Relaxation Spectrum		Retardation Spectrum	
	Time, τ_i	Modulus, G_i	Time, θ_i	Compliance, J_i
1	17	0.32	120	14
	5.3	0.35	8.1	0.44
	0.58	0.17	0.71	0.24
	0.05	0.06	0.05	0.07
2	16	0.43	120	14
	3.0	0.30	4.4	0.5
	0.30	0.13	0.35	0.18

functions. Certainly this is always possible, but the exact number of functions is always unknown. The minimum necessary number of exponents is determined by the quality of an experiment: their sum must give a curve deviating from the experimental data by no more than the error of measurement. Four exponents were taken for the selected probe relaxation curve (Table I, spectrum No. 1) and a quite satisfactory approach to the corresponding creep function was reached (Fig. 1).

Consequently the solution of the problem under discussion exists and can be found by the used method. But the sensitivity of this approach is also of great importance. A particularly interesting aspect of the problem is the role of a very short initial time period, because instrumentation effects are the most pronounced at the start of the relaxation, and the curve is least reliable when time values are small.

Let us examine the case omitting the initial part of the relaxation curve and using not four senior members of the exponential sum but three, two, or even one. In this situation the accuracy of the relaxation curve approximation decreases slightly, but (as one can see from Table II) the quality of any predictions of the creep curve deteriorates sharply

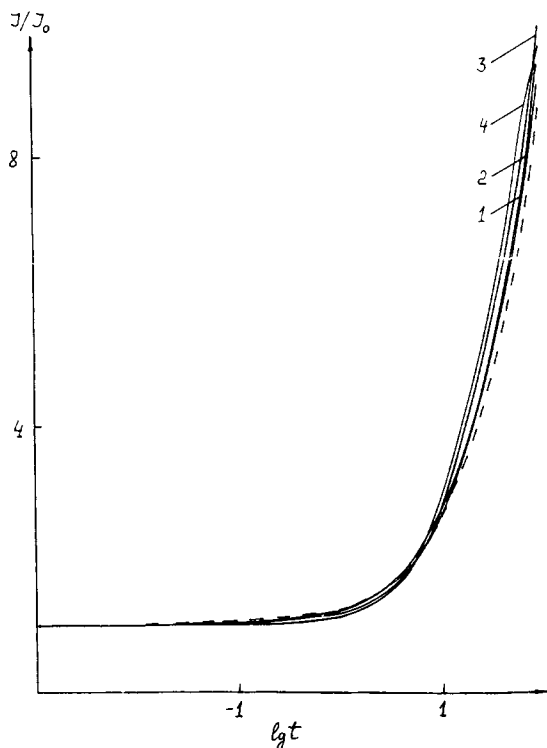


Figure 1 Results of calculation of the creep function, the relaxation curve being presented by the sum of exponents: one (4); two (3); three (2); or four (1) members.

Table II Influence of Decreasing the Number of Exponents in the Expansion on Predictions of the Creep Curve

Number of Exponents	Relaxation		Creep	
	Time Range	Δ , % ^a	Δ , %	Δ^{\max} , % ^b
4	10^{-3} - 10^2	1.2	3.3	5.8
3	10^{-1} - 10^2	1.2	5.6	8.4
2	10^0 - 10^2	1.5	11	16
1	10^1 - 10^2	0.7	13	27

^a Δ - average error.

^b Δ^{\max} - maximum error.

(Fig. 1). This is definitely connected with the contraction of the time scale for the relaxation data used for calculations. This result shows that the solution of the inverse problem depends on the quality of an initial experimental curve and of its approximation.

Inside the same boundaries of error for the same initial experimental data one can obtain different spectra using different methods of approximation. How can these influence the results of calculations? The answer to this question is based on an analysis of the spectrum No. 2 in Table I, which also describes the relaxation curve with a maximum deviation of less than 10%. The spectra Numbers 1 and 2 as well as the corresponding retardation spectra are rather different. Nevertheless in both cases the experimental (reference) and calculated creep functions are very close to each other (mean square deviation is equal to 4%). This means that the solution of the integral Equation (1) is fairly stable in respect to slight variations of the initial experimental data.

In accordance with the results of the computational experiment it is possible to say that

1. The integral problem of calculation of the creep function, on the basis of an experimental relaxation curve can have an adequate solution.
2. This solution can be obtained by expansion of the relaxation curve into the discrete sum of exponents.
3. The solution found by this method appears to be fairly stable in respect to some slight variations of initial experimental data.
4. The error in the creep prediction grows and becomes unacceptable if one gives up the initial part of the relaxation curve and uses a reduced number of exponential members.

Now let us try to answer the following question. If we approximate the relaxation curve by any function within the experimental corridor (which is set by the usual error of 10%), can we arrive at the correct creep function? There is another version of the same question: are the results of calculations insensitive to the choice of an approximation method?

Bearing in mind that a change in the number of exponents influenced the decomposition of the relaxation curve to only a small extent, one could expect to answer "yes", but in reality the answer is negative. To prove this, the relaxation kernel corresponding to the Kolhrausch function will be taken in lieu of exponents

$$R_k(t) = A_k \alpha_k \gamma e^{-\gamma t^{\alpha_k}} / t^{1-\alpha_k} \quad (0 < \alpha_k < 1) \quad (8)$$

It is possible to show that there are at least three sets of this function's parameters which present curves lying within the borders of the experimental corridor for a relaxation curve (Table III).

Again, what about the creep function? One can see from Table III that the results are strongly dependent on the choice of approximation parameters. None of the three sets of parameters gives the creep function with desirable accuracy with respect to the maximum error. The results of calculations are also shown in Figure 2, and one can see that the solution is unstable with respect to permissible experimental errors, and that slight variations in the initial conditions of this approximation method lead to a great divergence in final solutions.

Therefore the analytical approximation of the relaxation curve within experimental accuracy is a necessary but not a sufficient condition for the correct solution of the problem of calculating the creep function from the measured relaxation curve.

Table III Interrelation Between the Creep and Relaxation Functions^a

Number of Curve	Relaxation				Creep	
	γ	α_k	Δ , % ^b	Δ^{\max} , % ^c	Δ , %	Δ^{\max} , %
1	0.364	0.552	2.0	5.2	45	75
2	0.33	0.76	1.8	2.8	8	15
3	0.222	0.822	5.7	9.2	11	26

^a Approximated by Kolhrausch equation ($A_k = \text{const}$).

^b Δ - average error.

^c Δ^{\max} - maximum error.

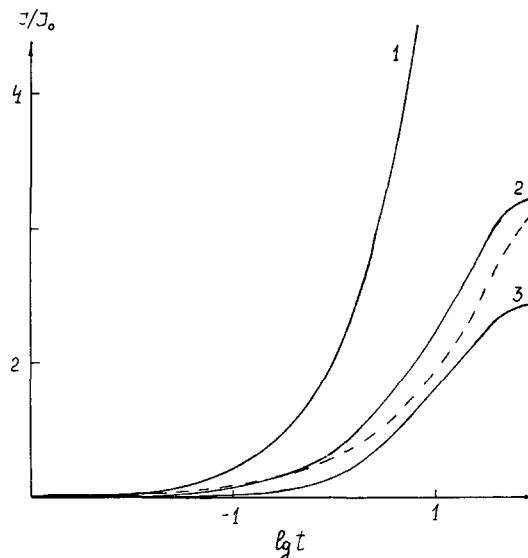


Figure 2 The results of calculation of the creep function, the relaxation curve being represented by Kolhrausch function. Numbers of the curve correspond to the ones in Table III.

EXPERIMENTAL

The experiments were made with an industrial grade of amorphous thermoplastic, PC Macrolon (Bayer).

Relaxation and creep functions were measured with the PC samples at the same temperatures. The levels on preset normal stress (in creep) σ_0 and strains (in relaxation) ϵ_0 were varied within the lim-

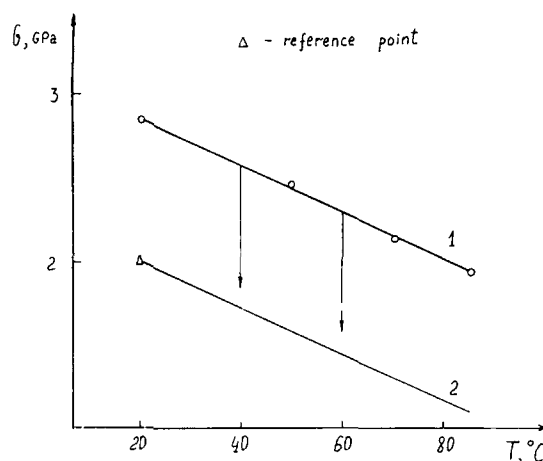


Figure 3 Method of determination of temperature dependence of the equilibrium elastic modulus (2) by parallel shift of the experimental instantaneous modulus-vs.-temperature curve (1).

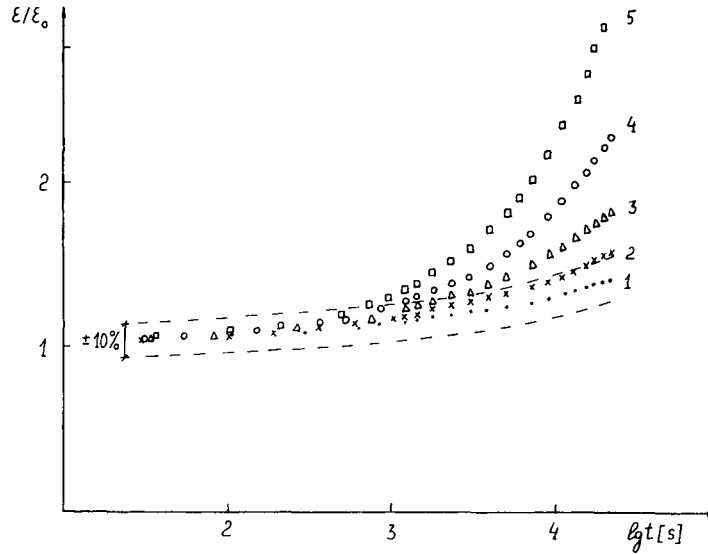


Figure 4 Normalized creep curves of PC at 50°C: (1) $\epsilon_0 = 1, \sigma_0 = 20$; (2) 1.5, 30; (3) 2, 36; (4) 2.5, 40; and (5) 3%, 42 MPa.

its shown in the experimental graphs discussed below. The temperature range was $T = 20-85^\circ\text{C}$.

The relaxation curves were determined by a Universal Testing machine Instron-1122 with an optional device which provided the capability of measuring stress versus time dependencies, strain being held strictly constant. The duration of relaxation was no more than 20 min.

The creep curves were measured by a homemade device with a tensometric transducer of deformation. All the experiments were made simultaneously for 10 samples. The error in stress during the relaxation and the relative divergence in extreme cases did not exceed 10%.

In addition to these direct measurements, creep functions were calculated from relaxation curves

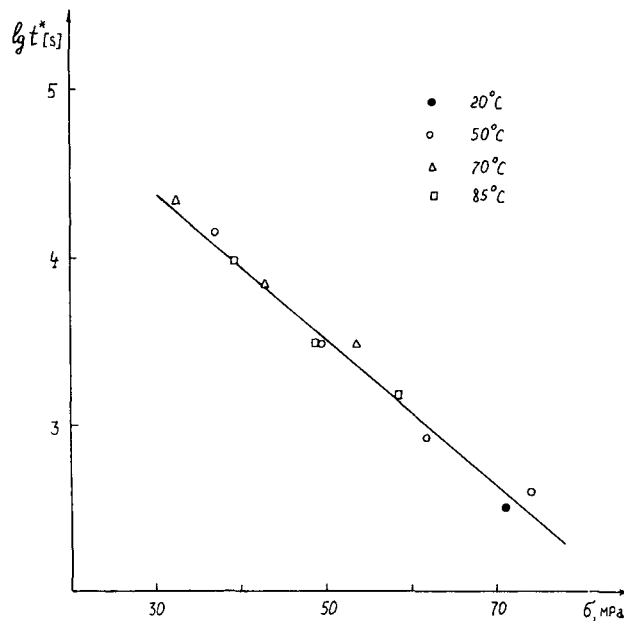


Figure 5 Dependence of critical time t^* on stress at different temperatures. Solid line represents approximation curve calculated according to Equation (9).

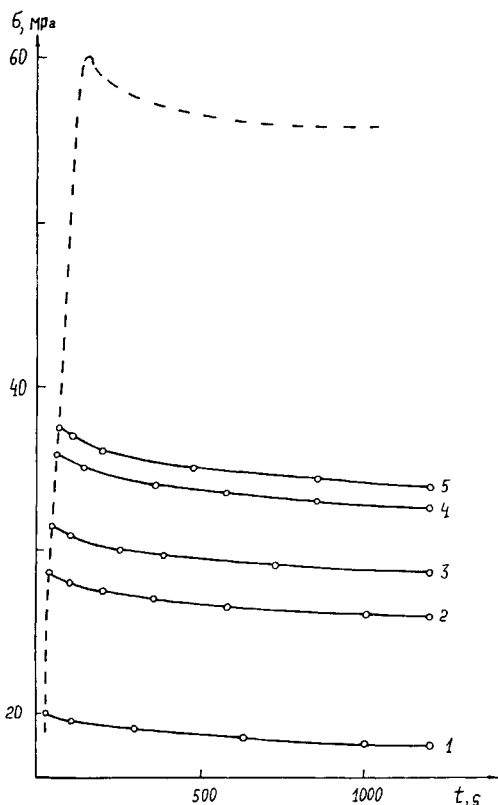


Figure 6 Experimental relaxation curves of PC at 50°C: (1) $\epsilon_0 = 1$; (2) 1.5; (3) 2; (4) 2.5; and (5) 3%. Dotted line represents the stress-strain curve (crosshead velocity being equal to 25 mm/s).

according to the procedure discussed above. This was done to compare the creep functions obtained by model calculations with some real experimental data, and to estimate the possible limits of the calculated creep function when extrapolated beyond the initial experimental range of relaxation.

DISCUSSION

The theoretically irreproachable method of expansion of relaxation curves into the sum of exponents immediately meets with difficulties on being applied to some real experimental data. The first and the most obvious of them is connected with the problem of determining equilibrium elastic modulus G_∞ at different temperatures which is impossible by direct measurements. Moreover it is quite unclear how to extrapolate relaxation curves to $t \rightarrow \infty$ in order to find G_∞ .

The instantaneous moduli G_0 and G_∞ can both be presented as different moments of the relaxation

spectrum of a substance⁴ and this means that an assumption about the analogous character of the temperature dependencies of these moduli can be made. It is then necessary to know only one reference value of G_∞ , as the temperature dependence of G_0 is rather easily measured. The reference point was taken where the best coincidence of the experimental and calculated creep curves occurs at $\epsilon_0 = 1\%$, $T = 20^\circ\text{C}$. The procedure is illustrated by Figure 3.

For the estimation of the limits of linear viscoelasticity behavior the creep curves were normalized by the instantaneous compliance J_0 . In this case the linear viscoelasticity range was taken, as usual, to be the deformation and stress fields in which the normalized creep curve did not depend on the preset stress; the assumption of PC creep linearity at $\epsilon_0 = 1\%$ was made.⁵ One can estimate the coincidence of curves measured at different stress levels only by taking into account the limits of experimental accuracy.

The experimental creep curves are shown in Figure 4. One can see that the initial parts of all the curves coincide, but that some deviations from the common field of points always appear when the experimental time scale becomes long enough. Hence, not only does the limit of linearity depend on stress but at a given initial stress nonlinearity appears after a certain time. This limiting (or critical) time t^* is the function of stress. This time t^* was considered as the point at which experimental curve deviation from linearity became greater than experimental accuracy (10%).

The dependence of critical time t^* on stress is shown in Figure 5. It can be described by the following empirical equation:

$$t^* = m \exp(-a\sigma) \quad (9)$$

where the stress-sensitivity factor $a = 0.101 \text{ MPa}$

Table IV Parameters of Discrete Relaxation Spectra, 50°C

Curve in Fig. 6	$\tau_1, \text{ s}$	G_1^a	$\tau_2, \text{ s}$	G_2	$\tau_3, \text{ s}$	G_3
1	3500	0.34	11	0.04	—	—
2	4000	0.28	58	0.06	2.8	0.02
3	3500	0.32	10.8	0.06	—	—
4	2700	0.29	11.2	0.095	—	—
5	2600	0.28	11	0.097	—	—

^a G_i are dimensionless, as the experimental relaxation curves were normalized.

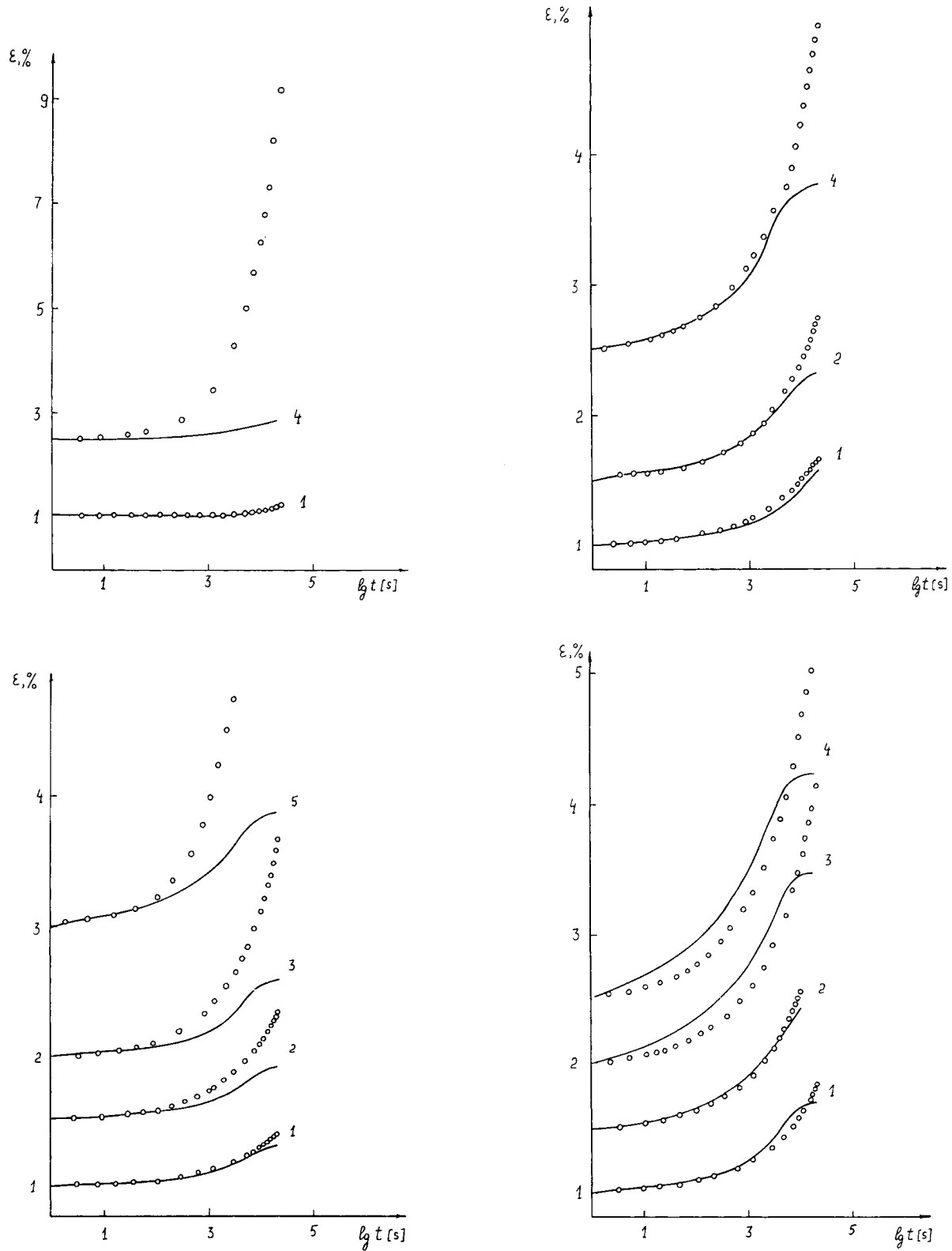


Figure 7 Creep curves of PC obtained by the expansion of a relaxation curve into the sum of exponents at 20° (a), 50° (b), 70° (c) and 85°C (d): $\epsilon_0 = 1$ (1), 1.5 (2), 2 (3), 2.5 (4) and 3% (5). Experimental creep curves are shown with points and calculated curves with solid lines.

and $m = 5.01 \times 10^5$ s. As one can see, the temperature does not influence the character of this dependence and a field of points at different temperatures exists. This result is rather strange and needs further experimental check and discussion. Nevertheless this is the main feature of the data in Figure 5. They allow the interpretation that some deviation from the linear viscoelastic behavior demands very low values of activation energy. Actually it is impossible to estimate the level of the activation energy in this case because of the natural scatter of experimental data, although the t^* values can be estimated albeit with a rather large error which is minimized by the log scale for time. Perhaps a critical value of t^* exists even for very low stresses, although these t^* values must be very high.

The next point of our discussion is the problem of the calculation of creep functions from relaxation curves, as shown in Figure 6. As was demonstrated above the calculation can be done by the expansion of a relaxation curve into a sum of exponents. In this case one need not treat the relaxation time values (presented in Table IV) as having some definite physical meaning but only as empirical parameters, especially as the number of functions is determined only by the quality (accuracy) of the experimental data.

The correlation of the calculated curves with the experimental creep functions is shown in Figure 7. One can see that the method of calculation indeed gives good results but only in the linear viscoelasticity range. Moreover the possibility of correctly predicting the creep function exists in the time scale ten-fold wider than the initial time range of relaxation (stresses in relaxation were measured during 10^3 s and predictions of the creep curve appeared to be valid up to 10^4 s). This result confirms the reliability of the exponential expansion of the relaxation curve as a predictor of the creep function in the linear viscoelasticity range. Meanwhile the problem of the limits of linearity and stress-versus-critical time curve has a separate meaning and can be solved by the way shown in Figure 5.

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NOMENCLATURE

a	Stress-sensitivity factor
G	Relaxation modulus
G_α	Equilibrium elastic modulus
G_0	Instantaneous elastic modulus
G_i	Ordinate of the relaxation spectrum
J	Creep compliance
J_0	Instantaneous compliance
J_l	Ordinate of the retardation spectrum
K	Creep kernel
m	Empirical constant
R	Relaxation kernel
T	Temperature
t	Time
t^*	Critical time
A, α, β, n	Parameters of Koltunov kernel
A_K, α_K, γ	Parameters of the kernel corresponding to Kolhtrausch function
σ	Stress
σ_0	Preset normal stress in creep
ϵ	Strain
ϵ_0	Preset strain in relaxation
η	Viscosity
τ	Time
τ_i	Characteristic relaxation time
ϕ	Relaxation function
ψ	Creep function
θ_l	Characteristic retardation time

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