

# EFFECT OF TEMPERATURE ON NONLINEAR CREEP OF SOME THERMOPLASTS

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## ABSTRACT

The deformational properties of polyoxymethylene, Nylon, PEEK, and polycarbonate were investigated. Nonlinearity in viscoelastic behaviour was revealed both in quasistatic tests with different constant strain rates and in short-term tensile creep tests in a wide range of applied stresses at room temperature. The analysis of stress-strain diagrams and creep isochrones showed different limits of linear behaviour and degree of nonlinearity of viscoelastic response. The degree of nonlinearity was evaluated as vertical deviation (by stress) of an isochrone from the tangent line which crosses coordinate axis at zero point. Taking into account absence of plastic deformations nonlinear creep was described by different models considering nonlinear viscoelastic responses. The cubic creep model and the model considering stress-time analogy principle are based on the Boltzmann and Volterra hereditary theory of viscoelasticity. Effect of temperature on nonlinear viscoelastic behaviour was investigated at a wide temperature range — from room up to 100 °C. The development of nonlinear effects considerably accelerates at simultaneous action of stress and temperature. Temperature dependence of the instantaneous compliances normalized to the corresponding compliances at room temperature was analyzed. Character of the dependencies for the materials is different: temperature growth leads both to reduction of stiffness (for polyoxymethylene) or its increase (for PEEK). Effect of temperature on viscoelastic behaviour of the materials also is not regular. Viscoelastic strain after 3 h creep with temperature growth  $\Delta T = 80$  °C increases 5 and 3 times for polyoxymethylene and PEEK and decreases for about 40% for Nylon, respectively. Temperature effect was taken into account by the time-temperature superposition principle passing to the reduced times. The temperature reduction function were obtained. The adaptable power law was also applied for the description of nonlinear creep. The calculations are in a good agreement with the experimental data for all the investigated materials.

## 1. INTRODUCTION

Deformability of thermoplastic polymers strongly depends on temperature. The time-dependent behaviour becomes more complicated when a polymer reveals nonlinear properties [1, 2]. This leads to necessity to elaborate methods for the determination of limits, when the material viscoelastic behaviour remains linear or contribution and/or development of nonlinear effects is unessential [3].

The models based on linear hereditary theory of viscoelasticity can be transformed and revised for nonlinear cases too [4, 5]. However, a limit of their use has to be determined due to complex effects appearing at simultaneous action of stress and temperature.

The objective of the present work was to compare effect of temperature on creep for some thermoplasts in a region of their nonlinear viscoelastic behaviour.

## 2. EXPERIMENTAL DETAILS

The investigated thermoplastic polymers are polyoxymethylene, Nylon, PEEK, and polycarbonate. The specimens had a dog-bone or bar shape and operative dimensions of 3x10x150 mm.

A series of quasi-static tests was performed at constant speed of displacement of the lower traverse of the MTS system: 0.1 and 5 mm/min, i.e. at constant strain rates  $\dot{\epsilon} = 1 \cdot 10^{-5}$  and  $6 \cdot 10^{-4} \text{ s}^{-1}$ , respectively.

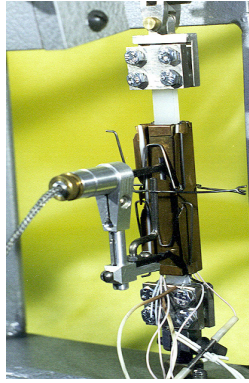
Short-term tensile creep tests were carried out according to ASTM D2990-01. Duration of creep and recovery tests were 3-5 h and 6-18 h, respectively. The tests were performed at room conditions in a wide range of applied stresses. Stress levels were chosen according to the yield stress  $\sigma^*$  of the materials (see Table 1). Strain measurements were made by extensometer with an accuracy of 0.2%.

“Table 1. Characteristics of the materials and conditions of the creep tests.”

Material	Yield stress $\sigma^*$ , MPa ( $\pm 10\%$ ), $T = 20\text{ }^\circ\text{C}$	Glass transition temperature $T_g$ , $^\circ\text{C}$	Creep stress $\sigma$ , MPa, $T = 20\text{ }^\circ\text{C}$	Creep temperature* $T$ , $^\circ\text{C}$
PEEK	100	326	15, 30, 45	20, 40, 60, 80, 100
Nylon	42	205	10, 15, 20, 25	20, 40, 60, 80, 100
Polyoxymethylene	64	153	10, 20, 30, 40	20, 40, 60, 80, 100
Polycarbonate [1]	60	157	14, 20, 30	20, 40, 60, 80

\*The tests were made at stresses highlighted in the 4<sup>th</sup> column.

The tests at elevated temperatures were carried out using an electrical mini oven attached to a specimen (see Fig. 1). The specimens were conditioned at a certain temperature at least 15 minutes prior to testing.



“Fig. 1. A specimen with mini oven prepared for a creep test at elevated temperature.”

Temperature measurement was made by a thermocouple connected with a control unit. The thermocouple was placed near the specimen surface. Temperature of the gage length of the specimen was maintained within  $1^\circ\text{C}$  by an automatic control of heating device.

### 3. THEORETICAL PART

For the description of the linear viscoelastic behaviour of the material in uniaxial tension under isothermal conditions, the integral form of the constitutive equations is used.

In the case of creep tests with stress history  $\sigma(t)$  for the strain  $\varepsilon(t)$  calculation one uses the equation of the Boltzmann — Volterra linear hereditary creep theory [6]

$$\varepsilon(t) = \frac{\sigma(t)}{E_0} + \int_0^t \sigma(s) K(t-s) ds, \quad (1)$$

where  $E_0$  is the instantaneous elastic modulus and  $K(t)$  is a creep function.

In the case of stress relaxation tests with strain history  $\varepsilon(t)$  the relation for the stress calculation is

$$\sigma(t) = E_0 \varepsilon(t) - \int_0^t \varepsilon(s) R(t-s) ds, \quad (2)$$

where  $R(t)$  is a relaxation function.

The creep and relaxation functions are independent on loading conditions if the behaviour is linear viscoelastic. These functions usually are expressed by a sum of exponents introducing a discrete relaxation (retardation) spectrum  $(A_i^c, \tau_i^c)$  or  $(A_i^r, \tau_i^r)$ .

For the simplest cases of creep and relaxation tests at  $\sigma$  or  $\varepsilon = \text{const}$  considering the independent action of the stress impulses (strain levels) applied at different time moments, the Eqs. 1 and 2 after integration take the form

$$\varepsilon(t) = \frac{\sigma}{E_0} \left[ 1 + \sum_{i=1}^k A_i^c \left[ 1 - \exp\left(-\frac{t}{\tau_i^c}\right) \right] \right], \quad (3)$$

$$\sigma(t) = E_0 \varepsilon \left[ 1 - \sum_{i=1}^k A_i^r \left[ 1 - \exp\left(-\frac{t}{\tau_i^r}\right) \right] \right] \quad (4)$$

In the case of quasi-static tests at a constant rate of strain  $\mathcal{E}$  for the description of  $\sigma - \varepsilon$  curves the following relation obtained from Eqs. 2 and 4 is applied:

$$\sigma(t) = \mathcal{E} \left[ E_0 t - \sum_{i=1}^k A_i^r \tau_i^r \left[ 1 - \exp\left(-\frac{t}{\tau_i^r}\right) \right] \right] \quad (5)$$

For the compliance Eq. 3 can be rewritten in the form

$$J(t) = J_0 + F(t), \quad (6)$$

$$F(t) = \sum_i A_i \left[ 1 - \exp\left(-\frac{t}{\tau_i}\right) \right], \quad A_i = \frac{A_i^c}{E_0}, \quad \tau_i = \tau_i^c, \quad (7)$$

where  $J_0$  is the instantaneous compliance and  $F(t)$  is the creep function.

Nonlinear viscoelastic behaviour one takes into account applying different models. Let's consider creep of nonlinear hereditary material at an uniaxial stress state. Then, it is necessary to take into account a joint effect of antecedent stress impulses at appropriate time moments  $s_j$ . For this purpose joint influence functions  $K_j$  of stress impulses has to be considered. In general case, we can write [4]

$$\begin{aligned} \varepsilon(t) = & \frac{\sigma}{E_0} + c_1 \int_0^t \sigma(s) K_1(t-s) ds + c_2 \int_0^t \int_0^t \sigma(s_1) \sigma(s_2) K_2(t-s_1, t-s_2) ds_1 ds_2 + \\ & + c_3 \int_0^t \int_0^t \int_0^t \sigma(s_1) \sigma(s_2) \sigma(s_3) K_3(t-s_1, t-s_2, t-s_3) ds_1 ds_2 ds_3 + \dots \end{aligned} \quad (8)$$

where  $c_j$  are material constants. Considering a joint influence of some stress impulses of the same time moment ( $s_1 = s_2 = \dots s_n$ ) Eq. 8 takes the form

$$\varepsilon(t) = \frac{\sigma}{E_0} + c_1 \int_0^t \sigma(s) K_1(t-s) ds + c_2 \int_0^t \sigma^2(s) K_2(t-s) ds + c_3 \int_0^t \sigma^3(s) K_3(t-s) ds + \dots \quad (9)$$

For materials with the same deformational properties in tension and compression only the terms containing stresses in odd powers in Eq. 8 are kept. In the simplest case, it can be assumed, that the influence functions are equals. Then, for  $\sigma = \text{const}$  the creep function is

$$F(t) = \int_0^t K_1(t-s)ds = \int_0^t K_3(t-s)ds = \dots \quad (10)$$

From mathematical point of view, the degree of nonlinearity is determined by a number of terms in Eq. 8 or maximal multiplicity of integrals. In the simplest case of nonlinear hereditary material the cub model can be applied for the creep description. Using Eqs. 9 and 10 for  $\sigma = \text{const}$  the following expression for creep compliance calculation is obtained (cub creep model)

$$J(t, \sigma) = J_0 + (c_1 + c_3 \sigma^2)F(t). \quad (11)$$

Parameters of the model Eq. 11 one determines empirically.

In some cases nonlinear viscoelastic behaviour is quite complex due to high degree of nonlinearity and difference of the influence functions. Then, the total creep equation includes a big number of additional parameters. This complicates a task of creep description and requires performing of additional tests. Therefore, sometimes it is convenient to consider stress dependence of the creep function Eq. 7. Stress level is considered as a factor which defines nonlinearity of a material. Quantitative characteristic of the nonlinearity is the stress-time reduction function  $a_\sigma(\sigma)$  [5]. Passing to the reduced time  $t \rightarrow t' = ta_\sigma$  Eq. 6 takes the form

$$J(t, \sigma) = J_0 + F(t, \sigma) \quad (12)$$

It has to be mentioned, that for some polymers instantaneous compliance is also a stress dependent function. Then, in Eqs. 11 and 12  $J_0(\sigma)$  has to be considered.

Another approach for the creep description is using of a power function [2, 7]. The linear creep response in a power-law form can be expressed as follows

$$\varepsilon(t) = \begin{cases} (J_0 + J_1 t^n) \sigma, & 0 \leq t \leq t_0 \\ J_1 [t^n - (t - t_0)^n] \sigma, & t \geq t_0 \end{cases} \quad (13)$$

where  $J_1$  and  $n$  are material parameters,  $t_0$  is the time moment when unloading occurs. For nonlinear creep description in Eq. 13 stress dependent functions  $J_0(\sigma)$  and  $J_1(\sigma)$  have to be used.

The effect of temperature is taken into account by temperature dependencies of the parameters of the models:  $J_0(T)$  and  $J_1(T)$ . Both the dependencies can be found experimentally. According to [2]

$$J_1(T) = G(T)J_1 = \frac{J_0(T)}{J_0(T_0)} J_1,$$

where  $T_0$  is a basic temperature (usually, it is a room temperature).

For the time-dependent function (viscoelastic response) the method of time-temperature equivalencies (TTE) [5] is used. According to the equivalence method, which is based on the use of factors accelerating the relaxation processes, temperature and time of deformation are

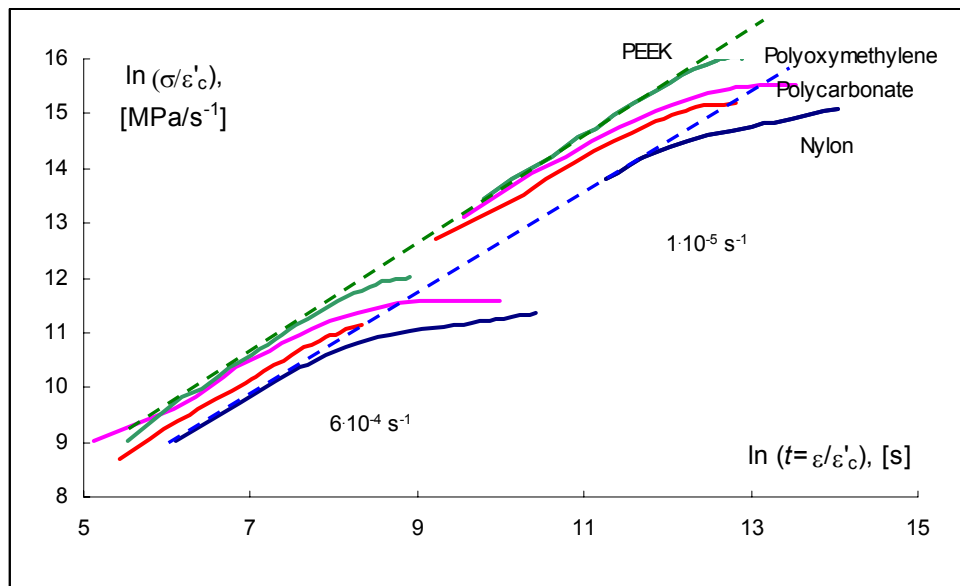
interdependent and relatively equivalent. The temperature effect on the creep (relaxation) is taken into account by passing to the reduced time  $t \rightarrow t'$ :

$$t' = ta_T \text{ or } t' = \frac{t}{a_T^{pl}} \quad (14)$$

where  $a_T$  and  $a_T^{pl}$  are functions of temperature reduction for the models described by Eqs. 12 or 13, respectively.

### 3. RESULTS & DISCUSSION

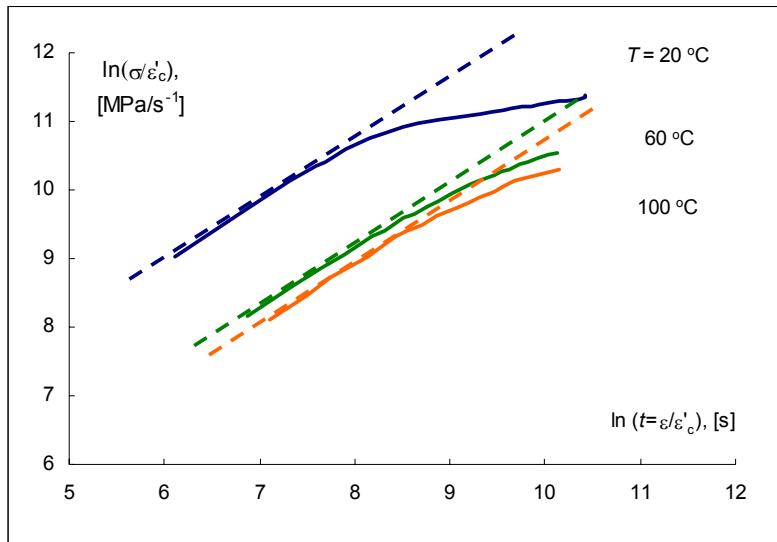
**Quasi-static tests.** Nonlinearity of viscoelastic behaviour of the investigated materials was evaluated by the results of stress-strain tests performed at different rates of strain. The experimental data are shown in Fig. 2, where so-called reduced (rate independent) stress and time are plotted in a double logarithmic representation.



“Fig. 2. The behaviour of the materials in quasi-static tests at different strain rates.

From the Eq. 5 follows that for a material with linear viscoelastic properties curves should fall on the same line. The deviations indicate to nonlinearity of the viscoelastic behaviour. Thus, Fig. 2 demonstrates nonlinear behaviour of the investigated materials, where the dashed lines correspond to the linear viscoelastic case [3].

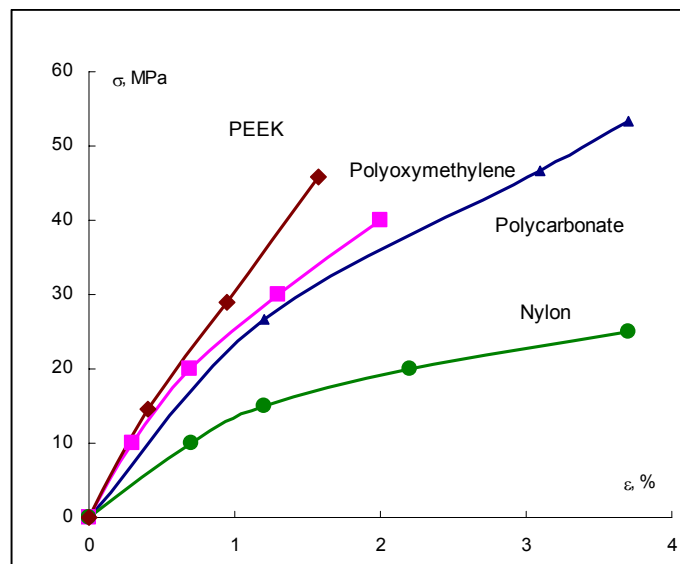
The effect of temperature on Nylon viscoelastic behaviour is shown in Fig. 3 as an example. The arrows indicates to a condition, when nonlinearity of the material behaviour becomes evident.



“Fig. 3. The behaviour of Nylon at  $\dot{\epsilon} = 6 \cdot 10^{-4} \text{ s}^{-1}$  and different temperatures.”

Temperature growth leads to a considerable decrease of the relative linear viscoelastic limit. This complicates the description of materials behaviour and leads to necessity to investigate viscoelastic properties in wide ranges of stresses and temperatures.

**Creep at different stresses.** The another indicator of physical nonlinearity of a material viscoelastic behaviour is type of creep isochrones. It is known, that linear elastic materials have straight-line isochrones. Typical creep isochrones of the materials obtained for the time moment 2.5 min are shown in Fig. 4 as an example.



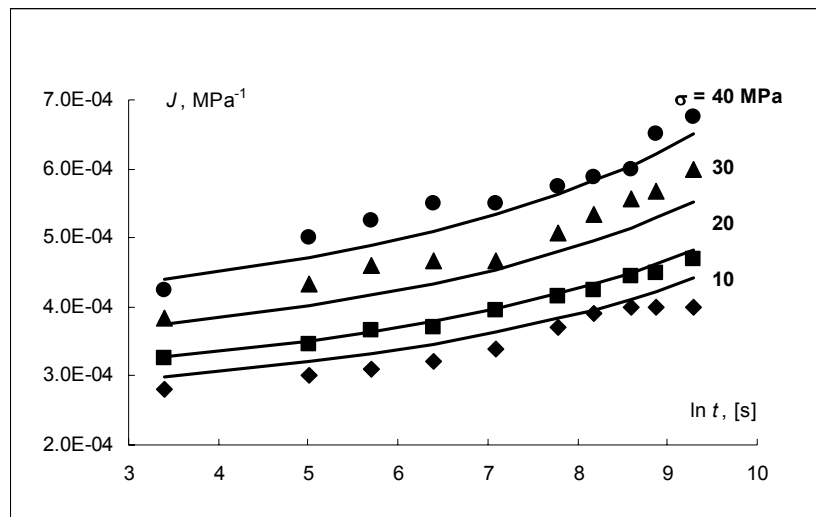
“Fig.4. Creep isochrones of the materials at  $t = 2.5 \text{ min}$ ,  $T = 20 \text{ °C}$ .”

The nonlinearity of the curves is evident. Together with determination of the limit of linear viscoelasticity the another method is suggested for comparison of the material behaviour. That is evaluation of the degree of nonlinearity of creep isochrones, which defines as vertical deviation (by stress) of isochrone from tangent line which crosses coordinate axis at zero

point. The determined values for stress level  $\sigma = 0.5 \sigma^*$  are 60, 43, 26, and less than 13% for Nylon, polyoxymethylene, PEEK, and polycarbonate, respectively.

The results of creep recovery tests showed that there are not residual strains for all the investigated polymers. This testifies to an absence of plastic deformations and, therefore, to a validity of use of the models for nonlinear creep description, which were considered in the previous section. The tests performed in a wide stress range (see Table 1) allowed to determine parameters of the models with an optimal accuracy. An appropriate model was fitted for each the material [7].

The cub model (see Eq. 11) gives the best approximation for the polyoxymethylene and polycarbonate [1] creep. That also follows from the character of isochrones (see Fig. 4), which are homothetic for different times and coincide at the scaling transformation. Experimental data of polyoxymethylene creep are shown in Fig. 5. The values of the model parameters determined by interpolation of isochrones are  $c_1 = 2.8 \cdot 10^{-4} \text{ MPa}^{-1}$  and  $c_3 = 9.1 \cdot 10^{-8} \text{ MPa}^{-3}$ . As shown in Fig. 5, the cub creep model and experimental data are in a good agreement.



“Fig.5. Creep of polyoxymethylene at different stresses. Lines are approximations by cub model.”

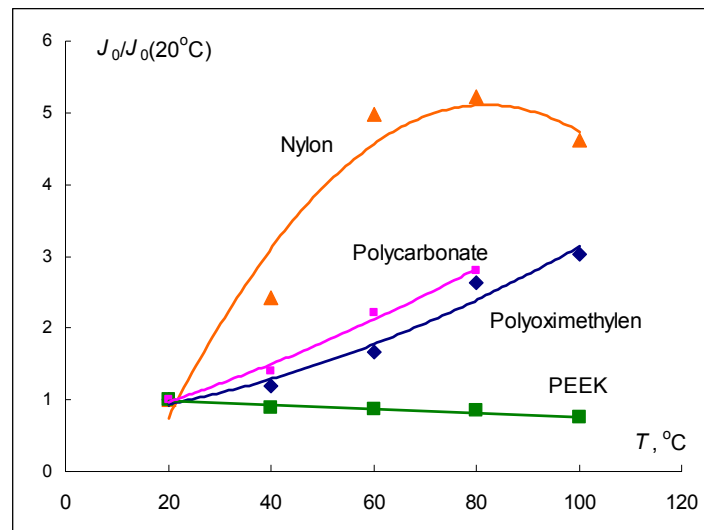
The best fit to experimental creep data of Nylon was achieved by applying the nonlinear viscoelastic model with the use of stress-time analogy Eq. 12. The stress-time reduction function  $a_\sigma(\sigma)$  was determined by horizontal shifting of the experimental creep curves along the logarithmic time  $\ln t$  axes referring to the basic creep curve for the load of  $\sigma_0 = 10 \text{ MPa}$ . The obtained dependence can be approximated by an expression  $\ln a_\sigma = 0.0085(\sigma - \sigma_0)^2 + 0.15\sigma$ , where  $\sigma$  unit is MPa.

From the results of quasi-static tests (Fig. 2) and creep isochrones (Fig. 4) it was seen that the viscoelastic behaviour of PEEK at the certain tests conditions is closed to linear. As expected, the model for the creep description should have minor deviations from the linear viscoelastic model. Thus, use of Eq. 6 together with the stress dependence of the instantaneous compliance gives satisfactory results. The instantaneous compliance (measured in  $\text{MPa}^{-1}$ ) as function of stress is  $J_0 = 2 \cdot 10^{-6} \sigma + 2 \cdot 10^{-4}$ .

The power law Eq. 13 was applied for the creep description. It showed a good agreement with the experimental data for all the investigated materials. It was possible to determine the stress dependent functions  $J_0(\sigma)$  and  $J_1(\sigma)$  from a series of the tests (see Table 1). The value of parameter is  $n = 0.3$  for all the materials. Note, that the power law is quite adaptable model for the creep description of materials with different deformation characters. However, this is

only an empirical model, which requires performing of a large number of tests for the determination of its parameters. Also it cannot explain the nature of physical process.

**Creep at different temperatures.** Effect of temperature on nonlinear creep of the polymers was investigated in short-term tensile creep tests at stress level  $\sigma < 0.5 \sigma^*$  ( $\sigma^*$  is yield stress at room temperature) at wide temperature range (see Table 1). Considerable differences in viscoelastic behaviour were revealed for the materials. Viscoelastic strain after 3 h creep with temperature growth  $\Delta T = 80 \text{ }^\circ\text{C}$  increases 5 and 3 times for polyoxymethylene and PEEK and decreases for about 40% for Nylon, respectively. Temperature dependences of instantaneous compliances normalized to the corresponding compliances at room temperature of the thermoplasts are shown in Fig. 6.

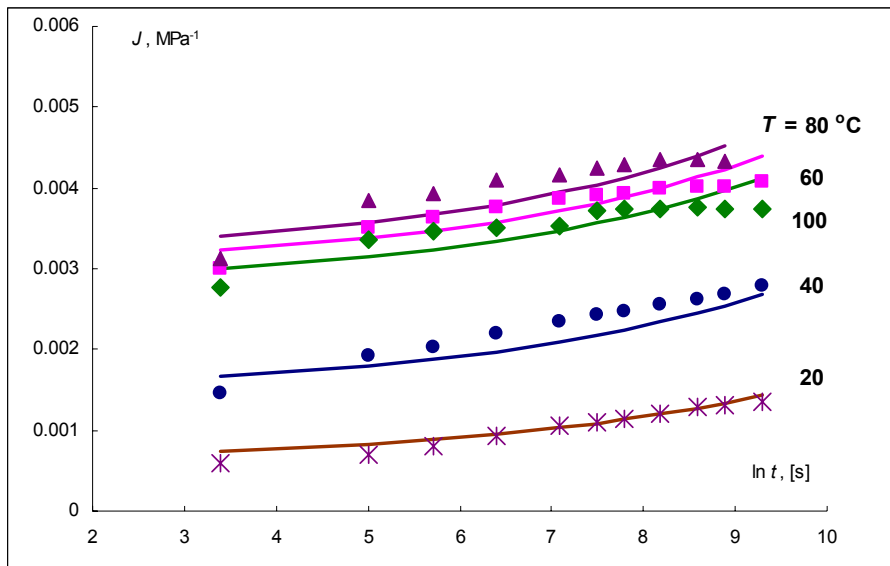


“Fig. 6. Temperature dependences of instantaneous compliances of the materials.”

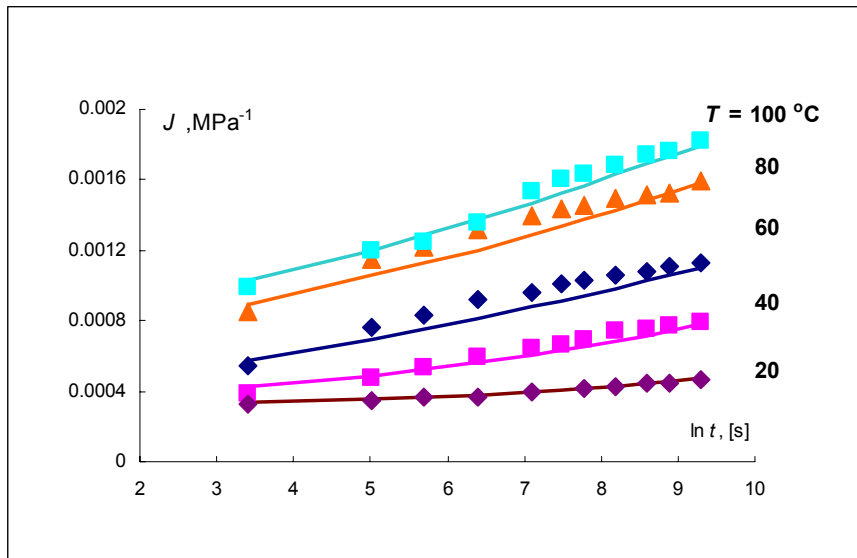
It is seen, that temperature growth leads both to increase of compliance (e.g. for polyoxymethylene) or it's reduction (e.g. for PEEK).

Creep of Nylon and polyoxymethylene are shown in Figs. 7 and 8 as examples. The corresponding models with use of the time-temperature superposition principle were applied for the creep description of each the material (here, they are the power law Eq. 13 and cub creep model Eq. 11 for Nylon and polyoxymethylene, respectively).



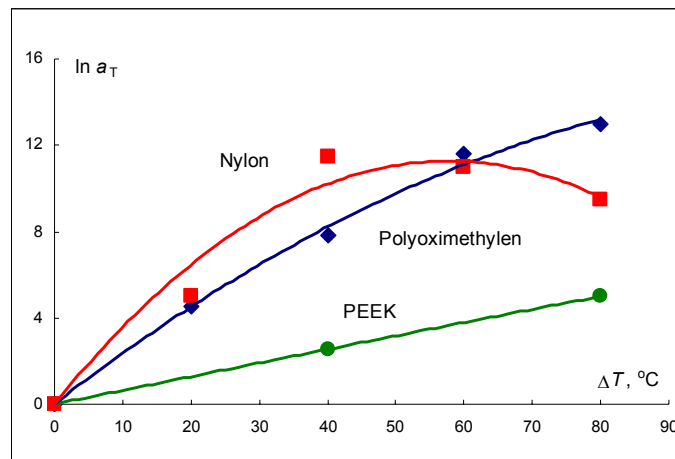


“Fig. 7. Nylon creep at different temperatures and  $\sigma = 10$  MPa. Lines are calculations by power law.”



“Fig. 8. Polyoxymethylene creep at different temperatures and  $\sigma = 20$  MPa. Lines are calculations by cub model.”

Temperature effect was taken into account passing on to the reduced times (see Eq. 14) and/or by horizontal shifting of the creep curves along the  $\ln t$  axes to a basic creep curve for  $T_0 = 20$  °C. The determined temperature reduction functions are shown in Fig. 9.



“Fig. 9. Temperature reduction functions,  $T_0 = 20$  °C.”

It has to be noted, that viscoelastic behaviour of Nylon at simultaneous action of stress and temperatures is quite complex and can be described only by the flexible power law. Use of the models based on the hereditary theory gives unsatisfactory results. Possibly, growth of temperature reducing the limit of linear behaviour (see Fig. 3) leads to the increase of development of nonlinear effects in the material. Obviously, that it requires a revise of the considered models, introducing of new parameters, and, therefore, performing of additional experiments.

#### 4. CONCLUSIONS

It is determined that the investigated materials reveal nonlinear viscoelastic behaviour in the considered ranges of stresses. The stress limits, when nonlinear effects in the material behaviour becomes evident, are estimated. It is suggested to evaluate the degree of nonlinearity by a shape of isochrones. The corresponding models for description of nonlinear creep are considered for each the material.

The effect of temperature on nonlinear creep of the materials is evaluated. Temperature increase leads to the development of nonlinear effects at lower stress levels. The method of time-temperature equivalencies is used for the description of nonlinear creep at elevated temperatures.

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