VIBRATIONAL CREEP OF POLYMER MATERIALS

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In the mechanics of deformed solids it is usually assumed that superposing small amplitude vibrations on a static load has no effect on the over-all characteristics of a material under strain. This hypothesis is reflected in the fact that the existing equations of state for the case of static loads with superposed small vibrations give deformation characteristics which differ little from the corresponding parameters of deformation processes taking place in the absence of excitations. At the same time, substantial changes in the deformation characteristics of a number of materials are observed under certain conditions after the application of alternating stresses of small amplitude. Reports on studies of creep of metals [1, 2], elastomers [3], and concrete [4] have been published, in which the fatigue curves obtained with small vibrations superposed on static loads lie above curves obtained for static loads corresponding to the maximum pulsating load level. Attempts have been made to explain this effect from the standpoint of the molecular-kinetic [3] and phenomenological [5] theories. Certain theoretical considerations and experimental data, discussed in this article, show that superposing a small dynamic component on a static load leads to an increase in the rate of creep of several polymer materials. This effect, which is due mainly to an increase in the polymer temperature as a result of dissipation of vibrational energy, differs from the "vibration effect" observed on elastomers by Slonimskii and Alekseev [3], in which the temperature rise due to the heat generated by vibrations plays no substantial part.

The vibrational creep of polymer materials observed in our experiments differed from that described in [3]. According to results obtained in [3], superposing a vibration component produces the same effect as increasing the static load at the moment indicated by an arrow (Fig. 1a). In our tests, the superposition of vibrations on a static load produces no immediate changes in the behavior of the material; it is only after a certain time (incubation period) that the creep rate $\dot{\varepsilon}$ begins slowly to increase. When the steady-creep stage is reached, $\dot{\varepsilon}$ is sometimes two to three orders larger than the value recorded before the superposition of vibrations (Fig. 1b); this increase in $\dot{\varepsilon}$ is accompanied by a substantial increase in specimen temperature. The delay in the acceleration of creep is evidently due to the fact that at the moment of the application of vibrations the material continues to deform elastically, so that the quantity of dissipated energy is small and the increase in specimen temperature slow. In the later stages, heating leads to a more intense energy dissipation which, in turn, generates more heat; as a result, avalanche-type acceleration of the creep rate takes place.

A characteristic feature of the vibrational creep of polymer materials under the conditions studied is that the stress σ is very little (1–2%) different from the static stress, so that the variation in stress may, in the first approximation, be neglected. The intense heating of a material in vibrational creep must be taken into account, however. The problem of heating of a specimen under a vibrational load was analyzed theoretically by Ratner and Korobov [6] under the assumption that the temperature gradient inside the specimen is negligibly small and that the heat-transfer resistance is concentrated at the specimen surface. The analysis presented below also takes into account the temperature distribution in the specimen interior.

§ 1. It is known that the elasticity of polymer materials is nonequilibrium in character, so that heat evolution during cyclic loading takes place in the entire specimen volume. In the first approximation, for sufficiently high vibration frequencies, the effect of the principal (static) load on heat evolution may be neglected. In this case, the quantity of heat evolved per unit time in a unit volume of a cylindrical specimen in tension is [7, 8]

$$W = {}^{1}/_{2}\omega\sigma_0^2 J''. \qquad (1.1)$$

Here σ_0 is the amplitude of the vibration component of tensile stress and J" the so-called loss compliance which, for a given material, depends on temperature T and frequency ω. In the case of amorphous polymers, this relation is represented by universal curves J" (ωa_T), where a_T is the ratio of relaxation times at various temperatures, which is given by the Williams-Landell-Furry equation [8]

$$\lg a_T = -\frac{c_1^\circ (T - T_0)}{c_2^\circ + (T - T_0)}. \qquad (1.2)$$

Here c_1° and c_2° are constants, and T_0 is the reference temperature. Experiment shows that, in the interval of practical interest, lg J" is linearly dependent on lg ωa_T, since one can obtain from (1.2)

$$J'' = \frac{K}{\omega^n} \exp \frac{\beta (T - T_0)}{1 + (T - T_0)/c_2^\circ},$$

where K, n, and β are constants. At small $(T - T_0)/c_2^\circ$, this relation may be approximately represented by

$$J'' = \frac{K}{\omega^n} \exp [\beta (T - T_0)]. \qquad (1.3)$$

Thus, for instance, using data from [7], one can show that the following relation is applicable to a plasticized poly-n-butylmethacrylate:

$$J'' = \frac{5 \cdot 10^{-6}}{\omega^{0.7}} \exp [0.26 (T - T_0)]; \qquad (1.4)$$

here temperature is in °K, frequency in cps, J" in cm^2/dyne, and T_0 = 227°K is the glass transition temperature. The Williams-Landell-Furry equation is not directly applicable to crystalline polymers, including caprolite which is the subject of the present investigation; there is, however, reason to suppose that the relation (1.3) is applicable to these materials in a certain range of practical interest.

Using Eqs. (1.1) and (1.3) and neglecting the temperature variation in the axial direction, we obtain the following equation for the heat balance of a cylindrical specimen:

$$\rho c \frac{\partial T}{\partial t} = \lambda \frac{1}{r} \frac{\partial}{\partial r} r \frac{\partial T}{\partial r} + \frac{K}{2} \sigma_0^2 \omega^{1-n} \exp\left[\beta (T - T_0)\right]. \quad (1.5)$$

Here ρ is density, c specific heat, λ thermal conductivity, and r instantaneous radius (measured from the specimen axis).

With a view to simplifying the analysis of the problem, we neglect both the temperature dependence of density, specific heat and thermal conductivity and the possible variation of stress amplitude σ_0 along the radius, associated with the variation in the elastic characteristics of the material; the latter is permissible, since the elastic modulus is relatively constant in the temperature range under consideration. In this way, the determination of the temperature variation along the radius and with time is reduced to solving Eq. (1.5) for the real initial and limiting conditions

$$\frac{\partial T}{\partial r} + \frac{\alpha}{\lambda} (T - T_0) = 0 \quad \text{at } r = r_0, \quad T = T_0 \quad \text{at } t = 0 \quad (1.6)$$

on the assumption that the heat radiation condition is satisfied at the specimen surface; (α—heat transfer coefficient; r_0—specimen radius).

Analysis of this boundary-value problem is similar to the analysis of stationary thermal explosion, first studied by Frank-Kamenetskii [9] (see also [10]). As is known, this problem has a certain nontrivial singularity, which has an interesting interpretation in the case of heat generated by vibration. To elucidate this singularity, it is advantageous to reduce Eq. (1.5) to dimensionless form; assuming

$$\beta (T - T_0) = u, \quad \tau = \frac{\varkappa t}{r_0^2},$$

$$\xi = \frac{r}{r_0}, \quad \delta = \frac{\beta K}{2\lambda} \sigma_0^2 \omega^{1-n} r_0^2,$$

we have

$$\frac{\partial u}{\partial \tau} = \frac{1}{\xi} \frac{\partial}{\partial \xi} \xi \frac{\partial u}{\partial \xi} + \delta e^u. \quad (1.7)$$

Assuming that the limiting conditions are stationary, it may be postulated that at $\tau \gg 1$, i. e., $t \gg r_0^2/\varkappa$, the solution should approach a steady-state solution which satisfies the equation

$$\frac{1}{\xi} \frac{d}{d\xi} \xi \frac{du}{d\xi} + \delta e^u = 0 \quad (1.8)$$

and the boundary condition

$$\frac{du}{d\xi} + \theta u = 0 \quad \text{at } \xi = 1. \quad (1.9)$$

The above-mentioned singularity of the problem consists in that the steady-state solution exists not for any values of δ, but only for $\delta \leq \delta_0$, when (as was shown in [11])

$$\delta_0 = \frac{8s}{(1+s)^2} \exp\left[-\frac{4s}{\theta(1+s)}\right],$$

$$s = \frac{2}{\theta} \left(\sqrt{1 + \frac{1}{4}\theta^2} - 1\right). \quad (1.10)$$

i. e., for

$$r_0^2 \leqslant \frac{2\lambda \delta_0 \omega^{n-1}}{\beta K \sigma_0^2} = r_*^2. \quad (1.11)$$

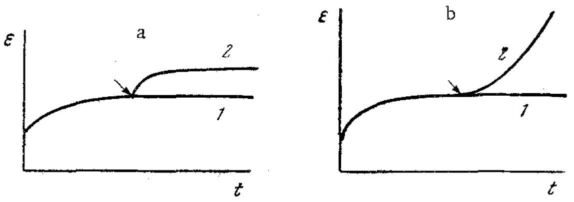

Fig. 1. a) Effect of vibrations observed in [3]; b) effect of vibrations due to heat evolution. 1) Creep curve (elastic aftereffect) of a polymer material in the absence of vibrations; 2) creep curve (elastic aftereffect) after the superposition of a vibration component. (The moment of application of vibrations is indicated by an arrow.)

In a special case $\delta_0 = 2$, if at the boundary $r = r_0$, $T = T_0$, i.e., $\alpha = \theta = \infty$. Inequality (1.11) shows that steady-state distribution of temperature is impossible when the specimen radius is larger than r_*. In this case, the specimen temperature will rise until the onset of thermal degradation, viscous flow, or other processes of polymer destruction. At $r_0 < r_*$ two steady-state solutions are possible (see, e. g., [10]), one of which (corresponding to more intense heating) is unstable; the latter fact was rigorously substantiated in [12]. At $r_0 = r_*$, the two solutions become one, and the distribution of reduced temperature u along the specimen radius is given by

$$u = \ln (8s / \delta_0) - 2 \ln (1 + s\xi^2), \quad (1.12)$$

so that the maximum reduced temperature u_* and the reduced temperature at the specimen surface u_{**} are equal to, respectively,

$$u_* = \ln \frac{8s}{\delta_0}$$
$$u_{**} = \ln \frac{8s}{\delta_0 (1+s)^2} = \frac{4s}{\theta(1+s)}. \quad (1.13)$$

If, following [6], one starts by averaging the temperature along the specimen radius and by assuming that all the heat-transfer resistance is concentrated at the boundary, the equation of the heat balance for a cylindrical rod becomes

$$\frac{dT}{dt} = \frac{\sigma_0^2 \omega^{1-n} K}{2pc} \exp\left[\beta (T - T_0)\right] - \frac{2\gamma}{\rho c \tau_0} (T - T_0), \quad (1.14)$$

where γ is the heat transfer coefficient. The unknown temperature satisfies this equation and the initial condition $T = T_0$. The expression for the critical specimen radius, above which steady-state temperature distribution is impossible, is in the form

$$r_* = \frac{4e^{-1}\gamma}{\sigma_0^2\omega^{1-n}K\beta} = \frac{1.47\gamma}{\sigma_0^2\omega^{1-n}K\beta}. \qquad (1.15)$$

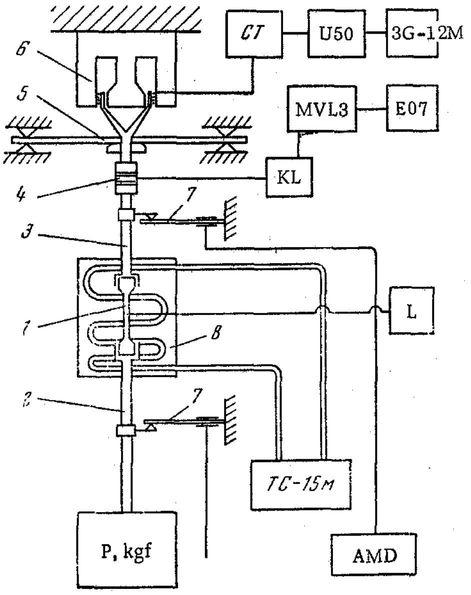

Fig. 2. Schematic of a machine for vibrational creep tests.

It should be noted that the approximation (1.3) cannot be used to describe vibration-induced heat evolution at too high temperatures, because the temperature dependence of J" passes through a maximum; this leads to the existence of a second stable steady-state process (see also [6]), in most cases unreal in the physical sense, because it corresponds to temperatures at which intense thermal degradation of polymers takes place. An analogous situation (including the existence of a physically unreal steady-state process at elevated temperatures) exists in the theory of thermal explosion, in which the exponential dependence of the reaction rate on temperature rise (postulated by Frank-Kamenetskii) at sufficiently high temperatures no longer satisfactorily approximates the Arrhenius equation.

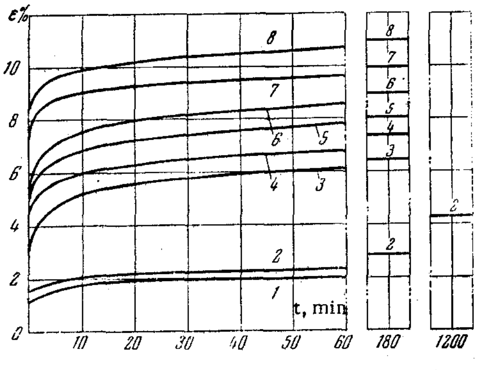

Fig. 3. Creep curves of caprolite under static load $\sigma = 3$ kg/mm². 1, 2) T = 20° C; 3, 4) T = 40° C; 5, 6) T = 60° C; 7, 8) T = 80° C.

The following sections describe the results of experiments which show that in the case of polymer materials a situation is possible when the increase in the rate of creep after the application of vibrations is mainly a result of the increase produced in the specimen temperature by the dissipation of energy.

§2. The creep tests were carried out on a testing machine constructed in the Mechanical Department of the Research Institute at Moscow State University; a schematic of the machine is shown in Fig. 2. The static load was applied by a weight P suspended on a connecting rod 2 which, in turn, was secured to the specimen 1. The load was transmitted through a connecting rod 3 and a piezo-probe 4 to a beam 5. The vibrational load component was excited by a dynamic head 6. Alternating (sinusoidal) emf for the excitation of vibrations was generated by 3G-12M audio-frequency oscillator and transmitted through a U50 amplifier and a CT matching transformer to the coil of the dynamic head rigidly attached to the beam 5.

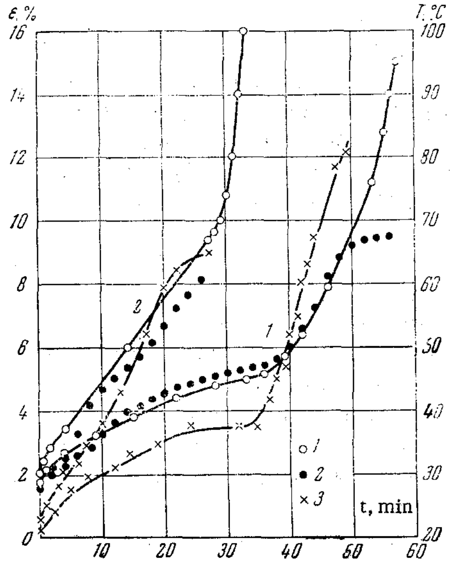

Fig. 4. Vibrational creep curves of caprolite: 1) experiment; 2) calculation from formula (3.3); 3) variation in specimen temperature.

The dynamic load component was measured with a barium titanate piezocrystal differential probe 4 which converted the force pulses into electric signals. The alternating emf generated by the piezo-probe was transmitted to a cathode follower and recorded with the aid of a MVL-3 millivoltmeter and a EO-7 oscillograph. The oscillograph was provided to observe the form of the dynamic load pulses.

The variation in the specimen strain was measured (utilizing the displacement of shackles) with the aid of cantilever beams 7, which were provided with wire resistance strain gauges. The free ends of these beams were acted on by stops attached to the connecting rods 2 and 3, whose strains were negligibly small in comparison to the strain of the specimen. Displacement of these rods produced changes in the bending diflection of the cantilever beams; the resulting signal from the strain gauges was transmitted to an automatic bridge AMD which recorded on a graph paper the differences between the displacements of rods 2 and 3, i.e., the specimen strain (or, more accurately, the static strain component). A dismountable heating chamber was provided for tests at elevated temperatures. Heating was done by the passage of a heat-transfer agent flowing through a spiral tube; the heat-transfer agent, circulating in a closed circuit, was supplied from a thermostat TC-15M.

Figure 3 shows the results of creep tests on caprolite specimens at 20°, 40°, 60°, and 80° C, under a constant stress $\sigma = 3$ kg/mm^2 (calculated for the initial cross section). The specimens were in the form of cylindrical rods 6 mm diam., with a 60 mm long gauge portion. The results of creep tests obtained for identical caprolite specimens with a dynamic load was superposed on the static load $\sigma = 3$ kg/mm^2 (40% of the UTS) are shown in Fig. 4. The dynamic load frequency was 200 cps, its amplitude 0.06 kg/mm^2, i.e., 2% of the applied static load. The initial ambient and specimen temperature was 20° C. The variation in the temperature of specimens under a combined influence of static and dynamic loads is illustrated by curves 3 in Fig. 4. The temperature was measured in the middle of the specimen gauge portion with a copper-constantan thermocouple, made of 0.03 mm diam. wires. The difference in the rate of heating of specimens 1 and 2 was mainly a result of differences in the thermal insulation of these specimens. (Thermal insulation was used to equalize the specimen temperature both in the longitudinal and in the radial direction; without insulation, the temperature gradient along the specimen radius would be considerably steeper.)

Comparison of the results reproduced in Fig. 3 and 4 gives no answer to the question whether the effect of vibration on the rate of creep of polymers is only due to the increase in the specimen temperature and a corresponding reduction in its strength, or whether another temperature-independent mechanism operates. The point is that data shown in Fig. 3 were obtained at constant test temperatures, while those reproduced in Fig. 4 were obtained for specimens whose temperature was continuously rising. The question whether or not a temperature-independent vibration effect exists could be settled by experiments of two kinds. One could, for instance, carry out tests with superposed vibrations and maintain the specimen temperature constant by cooling; comparison of results obtained under these conditions for specimens under equal static loads with and without superposed vibrations should show whether vibrations alone can produce the effects observed. (Tests of this kind were carried out by Lokoshenko and Shesterikov on duralumin specimens, in the case of which vibrational creep divorced from temperature vibrations was observed.) One could also carry out tests with and without superposing vibrations on identical static loads, ensuring that the temperature of specimens under static loads varied in the same way as that of specimens under pulsating loads. Unfortunately, carrying out tests of either kind on polymer specimens involves considerable difficulties. Consequently, instead of running tests under static load at variable temperatures, we constructed theoretical creep curves of this kind, using creep test results obtained at constant temperatures and assuming the temperature variation to be represented by curves 3 in Fig. 4. Some theoretical considerations, on which the construction of these curves was based, are discussed in the following section.

§3. Let us analyze the deformation process. Following the known kinetic concepts of deformation [13, 14] we shall write the equation of the creep strain rate in the form

$$\frac{d\varepsilon_c}{dt} = F(\varepsilon_c) \exp \frac{-(U-\gamma\sigma)}{RT}. \tag{3.1}$$

Here ε_c is the creep strain, U the activation energy, σ the stress, T the temperature, R the universal gas constant, γ the material constant, and t the time. This expression assumes an Arrhenius dependence of the strain rate on temperature, a linear dependence of U on σ, and a certain dependence of the strain rate on accumulated strain. In a general case, when σ and T are time-dependent, the integral of (3.1) will be

$$\chi(\varepsilon_c) = \int_0^{\varepsilon_c} \frac{d\varepsilon_c}{F(\varepsilon_c)} = \int_0^t \exp - \frac{(U-\gamma\sigma)\,dt}{RT}, \tag{3.2}$$

or, in inverted form,

$$\varepsilon_c = \Psi\left\{\int_0^t \exp - \frac{(U-\gamma\sigma)}{RT}\,dt\right\}. \tag{3.3}$$

Here the function Ψ is the inverse of χ. In the special case of constant σ and T during the entire deformation process, (3.3) becomes

$$\varepsilon_c = \Psi\left\{t \exp - \frac{(U-\gamma\sigma)}{RT}\right\}. \tag{3.4}$$

Equation (3.4) was first derived in [15]. Based on the above relations, a simple method of determining the function $\Psi(x)$ and parameters U and γ can be proposed. This method consists in the following.

Creep tests are carried out at several constant temperatures T_1, T_2, ..., at a constant stress σ to obtain a series of curves

$$\varepsilon_c = \varepsilon_1(t), \qquad \varepsilon_c = \varepsilon_2(t), \ldots \tag{3.5}$$

If the reasoning on which Eq. (3.3) and (3.4) are based is correct, it should be possible to obtain each of these curves from another by conformal transformation of the time axis, so that

$$\varepsilon_1(t) = \varepsilon_2(a_T t) = \ldots \tag{3.6}$$

From (3.4) it follows that

$$a_T = \exp \frac{-(U-\gamma\sigma)}{RT_2} \Big/ \exp - \frac{(U-\gamma\sigma)}{RT_1} = \exp \frac{-(U-\gamma\sigma)(T_1-T_2)}{RT_1T_2} \tag{3.7}$$

so that, knowing the value a_T from experiment, the reduced activation energy U-$\gamma\sigma$ can be easily found from (3.7). Finally, knowing U-$\gamma\sigma$ and using any one of curves (3.5), we obtain the function $\Psi(x)$, after which Eq. (3.3) is used to construct the curve representing the variation in strain at variable stresses and temperatures.

This method was used to construct curves $\varepsilon(t)$; the time-dependence of T was assumed to be that determined by vibrational creep tests. The results plotted in Fig. 4 (blackened circles) show the behavior of specimens under static load.

Data in Fig. 4 show that curves 2, constructed by the above described method, almost coincide with curves 1 obtained for pulsating loads. It may therefore be concluded that the increase produced in the rate of creep by superposing vibrations on static loads is due mainly to changes in the material strength associated with heat evolution and resultant temperature rise.

At certain values of the activation energy U$-\gamma\sigma$ it was observed that this property is temperature-dependent. This result is not a contradiction of published reports (e.g., [16]) that varying T produces changes in the activation energy for relaxation processes. In our calculations we used a certain "effective vibration energy," which was determined from, for instance, creep curves at 20° and 40° C, or 40° and 60° C, etc.; the difference between values so obtained and the actual values at given temperatures cannot lead to serious errors in the construction of theoretical curves.

The relations used above in the analysis of experimental data represent, from the point of view of the phenomenological theory of creep, a variant of the theory of strain hardening. It should be noted that Eq. (3.1) is valid for not too low stresses only.

In the final stages of our creep tests, the formation of a neck, similar to the necking associated with "cold flow" and described by Kargin and Sogolova [17], was observed. Since the theories cited in this article make no claims to describe processes that take place in the neck, there is no reason to suppose that close agreement between experimental and theoretical curves (curves 2 and 1 in Fig. 4) would also be observed in the large strain range, i.e., in the presence of necking. This view is supported by the fact that the theoretical curve constructed for specimen 2 deviates sharply from the corresponding experimental curve at large strains. A theory of neck propagation was previously formulated in [18].

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