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UTILIZATION OF THE THERMAL STRAIN OF SOLIDS FOR DETERMINING THE CONSTANTS OF INTERNAL HEAT TRANSFER OF SOLID-PHASE POLYMERS

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The article describes a rapid dilatometric method, absolute in instrumental provisions, of determining the heat-transfer coefficients, thermal diffusivity, coefficients of thermal expansion and of volumetric heat capacity of polymers.

The rapid dilatometric method of determining the thermal diffusivity of solid-phase materials of polycrystalline structure, described by a number of authors [1, 2], can be used successfully for the quantitative determination of the constants of thermal conductivity λ and of thermal diffusivity a, and also for studying the temperature dependence of the coefficient of thermal expansion β and of the volumetric heat capacity c_V correlated with the heat transfer constants by the known identity [3]:

$$\lambda = ac_V. \tag{1}$$

For this purpose it is expedient to make use of the special features of the kinetics of thermal expansion of cylindrical specimens (whose radius R is one and a half to two orders of magnitude smaller than their length L) in the regime of heating of the third kind and subsequent cooling from the lateral surface by a stream of coolant with constant temperature of the core of the stream [1].

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Solid-phase polymers are heated by a small electric wire heater mounted on the axis of the specimen. Simultaneously the change ΔT_I is recorded with the aid of Chromel–Copel thermocouples pressed into the surface of the specimen, as well as the rate of change of the volume (length) of the specimen W (with running absolute elongation Δl_I). The rate of increase of the volume W_H depends on the coefficient of thermal expansion β, the power P released in the small heater, and on the total power of all kinds of thermal losses Q [4]:

$$W_H = \frac{\beta}{c_V}(P - Q). \tag{2}$$

The period of heating the specimen in the regime of the third kind is suitable both for measuring the volumetric heat capacity c_V and for studying its temperature dependence. For this purpose heating was carried out under atmospheric conditions, and the rate of increase of the temperature $v = \partial T/\partial t$ on the axis of the specimen, the rate of elongation W_H, and the heating power P were measured immediately before switching off.

At the instant directly preceding the switching off of the heater and the instant directly after it the power of all kinds of thermal losses Q (convective, contact, etc.) is the same. Therefore the rate of decrease of the dimensions of the specimen W_0 immediately after switching off of the heater is determined only by the decrease of the total enthalpy of the specimen [4]:

$$W_0 = -\frac{\beta}{c_V}Q. \tag{3}$$

By Eqs. (2) and (3) we can calculate that part of the power p that ensures increase of the temperature of the specimen in the heating regime of the third kind directly at the instant of switching on the heater:

$$p = \frac{W_H}{W_0}P. \tag{4}$$

A remarkable property of the heating regime of the third kind is the constant rate of change of the temperature $\partial T/\partial t$ at any point of the bulk of the specimen V. Therefore the rate of change of the mean integral temperature $\frac{d}{dt}\overline{\Delta T}(r, z, t)$ has the same property:

$$\frac{d}{dt}\overline{\Delta T}(r, z, t) = \frac{d}{dt}\int_V T(r, z, t) = \pi R^2 L v. \tag{5}$$

It should be noted [5] that the rate of thermal expansion (2) is proportional to the rate of change of the mean integral temperature (5):

$$W_H = \beta\frac{d}{dt}\overline{\Delta T}(V) = \beta\pi R^2 L v. \tag{6}$$

It was shown above that the sensor of the rate of change of the temperature v is a thermocouple, and in case of axial symmetry of the temperature field the position of the thermocouple on the surface of the specimen is immaterial. The electronic device ensuring a constant rate of change of the mean integral temperature (the current intensity I_t in the electric heater and the voltage drop u_t in it — both magnitudes change with time t — see Fig. 1) guarantees, on account of equality (6), that the rate of thermal expansion W_H is also constant.

In the general case the rate of change of the mean integral temperature is determined by the "true" heating power p, which differs from the power P released in the heater in consequence of the thermal losses Q, and for the actual specimen it is described by the balance equality

$$c_V\frac{d}{dt}\overline{\Delta T}(V) = p. \tag{7}$$

Reverting to formula (5) and assuming that dilatometry in the heating regime of the third kind admits instantaneous switching off of the heating current with the corresponding measurement of the rates of change of the volume of the specimen at that instant, we can easily find c_V from equalities (2)-(4), (6), and (7):

$$c_V = \frac{P}{\pi R^2 L v}\cdot\frac{W_H}{W_0}. \tag{8}$$

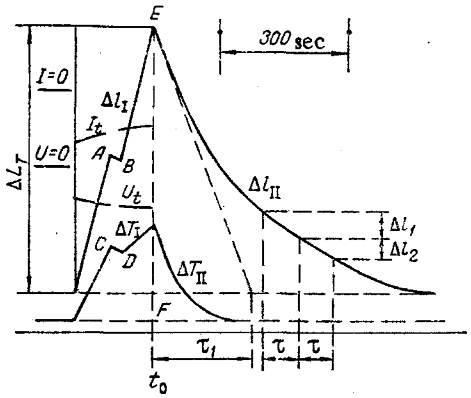

Fig. 1. Oscillogram of the heating and cooling of a specimen of polymethyl methacrylate in the temperature range 30-80°C: I = 0 and U = 0 are the zero lines of current intensity and voltage drop, respectively; $\Delta l = 0$ and $\Delta T = 0$ are the zero lines of the change of dimensions and of temperature, respectively; AB and CD express, respectively, the reduction of the dimensions of the specimen and its temperature drop on account of all kinds of thermal losses at the time of switching off of the small electric heater; EF is the line of concluding the heating and beginning the cooling by the coolant; ΔT_{II} is the curve of changes of the surface temperature in cooling; ΔL_T is the maximum absolute change of dimensions of the specimen within which together with the time interval τ_1 the rate W_1 lies.

Many times repeated switching on and off of the heater makes it possible to investigate the temperature dependence of the heat capacity c_V. At the same time relations (5) and (6) make it possible, with a slight radial temperature gradient, to study the temperature course of the coefficient of thermal expansion because $v = \frac{1}{V}\frac{d}{dt}\,\overline{\Delta T}(V)$.

The concluding part of the experiment begins when after a number of successive switchings on and off of the heating current, the heater at some instant t_0 (Fig. 1) is finally switched off, and at the same instant the lateral surface of the specimen is brought into contact with the stream of coolant which has constant temperature. A characteristic feature of the initial stage of reduction of dimensions of the specimen is that the initial rate of the decrease of length W_1 is correlated by a simple dependence with the heat capacity c_V and the heat exchange coefficient α between the core of the stream and the lateral surface of the specimen [2]:

$$\frac{\alpha}{Rc_V} = \frac{W_1}{2\Delta L_T}, \tag{9}$$

where ΔL_T is the absolute change of length of the specimen from the instant t_0 to the complete termination of thermal expansion in consequence of the equalization of the temperature of the entire specimen and of the core of the stream of coolant.

At the concluding stage of the temperature changes in the specimen, when the current change (decrease) of the dimensions Δl_{II} obeys an exponential dependence on time [6], it makes sense to register two successive elongations Δl_1 and Δl_2 during equal and adjacent time intervals τ (Fig. 1) on condition that the instant t of this measurement was itself chosen arbitrarily on the exponential curve Δl_{II}. Then

$$\Delta l_2 = A\left[\exp\left\{-\frac{\mu_1^2}{R^2}a(t+\tau)\right\} - \exp\left(-\frac{\mu_1^2}{R^2}at\right)\right], \tag{10}$$

TABLE 1. Values of the Root μ_1 in Dependence on the Values of b and $f(\mu_1)$

b	88	2,61	1,26	1,09	0,75	0,57	0,52	0,2	0,05	0
$f(\mu_1)$	208	5,06	2,57	2,07	1,09	0,57	0,26	0,1	0,05	0
μ_1	2,4	2,2	2,0	1,9	1,5	1,0	0,5	0,2	0,1	0

where A is some constant containing geometric and thermophysical constants [2]; μ_1 is the root of the equation [2]:

$$\mu_1 = \frac{\alpha R}{\lambda} \frac{I_0(\mu_1)}{I_1(\mu_1)}, \tag{11}$$

where $I_0(\mu_1)$ and $I_1(\mu_1)$ are Bessel functions of zero and first order.

The elongation of the specimen within the time interval τ immediately preceding the instant t is described by an analogous equation [2]:

$$\Delta l_1 = A\left[\exp\left(-\frac{\mu_1^2}{R^2} at\right) - \exp\left\{-\frac{\mu_1^2}{R^2} a(t-\tau)\right\}\right]. \tag{12}$$

It is appropriate to rewrite relation (11) using the empirical parameter b calculated from the characteristics of equality (9):

$$\mu_1 = \frac{1}{b} \frac{I_1(\mu_1)}{I_0(\mu_1)} = \frac{\alpha R}{ac_V} \frac{I_1(\mu_1)}{I_0(\mu_1)}. \tag{13}$$

From parameter b we can easily find the first root of Eq. (13) through the tabulated function $f(\mu_1) = \frac{I_1(\mu_1)}{I_0(\mu_1)}$ (see Table 1). Here and henceforth it is assumed that the changes of length and volume of the specimen are adequate, i.e., we deal with isotropic objects of investigation.

On the whole it is fairly simple in practice to bring the lateral surface of the specimen uniformly and simultaneously into contact with the stream of coolant if a sprinkler jacket arranged coaxially with the specimen is envisaged in the dilatometric installation (Fig. 2). The jacket is a cylindrical hollow body on whose inner surface the required number of holes were drilled for the injection of coolant which fills the jacket under a pressure of 1 abs. atm.

It follows from above that both stages of thermal effect on the specimen yield information: the initial (heating) stage whose data predetermine the calculation of volumetric heat capacity and of the coefficient of thermal expansion; and the concluding (exponential) stage ensuring the calculation of the first root of the Bessel equations of zero and first orders (and thus the determination of the thermal diffusivity). In particular, for calculating thermal diffusivity, it is expedient to use equalities (10) and (12). But first it is advisable to introduce the notation:

$$\frac{\Delta l_1}{\Delta l_2} = n, \quad \exp\left(\mu_1^2 \frac{a}{R^2}\tau\right) = y. \tag{14}$$

If we divide equality (12) by Eq. (10) and use the notation (14), we obtain after elementary transformations that

$$y^2 - (n-1)y - n = 0. \tag{15}$$

It is easy to see that the quadratic equation (15) has two roots: $y_1 = n$ and $y_2 = -1$. The second root has to be discarded since it has no physical meaning. Consequently, reverting to the initial notation (14), we obtain the equality

$$\mu_1^2 \frac{a}{R^2}\tau = \ln\frac{\Delta l_1}{\Delta l_2}, \tag{16}$$

which we are perfectly entitled to regard as the formula for calculating thermal diffusivity. Here it is important that the coefficient a is not calculated from the data of temperature measurements but only by using the kinetic curves of thermal strain of the specimens analyzed directly according to the oscillogram of cooling in arbitrary scale units. Yet another advantage of the method should be emphasized: the rapidity and the nature of the

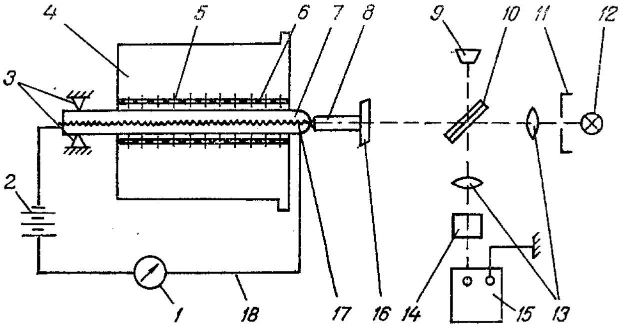

Fig. 2. Block diagram of the optical-interference dilatometer: 1) wattmeter; 2) current source (accumulator battery); 3) collet for gripping the specimen; 4) coolant tank; 5) strip between the surface of the specimen and the holes of the sprinkler; 6) sprinkler; 7) specimen; 8) quartz rod transmitting the motion of the specimen; 9) one of the mirrors situated in the arms of the interferometer; 10) translucent plate; 11) collimator; 12) source of monochromatic radiation (laser); 13) lenses situated in different arms of the interferometer; 14) photomultiplier FÉU-17; 15) loop oscillograph; 16) mirror mounted on the quartz rod; 17) small electric heater; 18) electric heating circuit.

measurements which is absolute as regards instrumental provisions. Moreover, slight improvements in design concerning the method of heating the specimens on the known model of the lever and optical (or optical-interference — see Fig. 2) dilatometer do not make it unsuitable for its traditional purpose, viz., the investigation of the temperature behavior and anomalies of the coefficient of thermal expansion (by formula (6) that was obtained above).

Thus the values of volumetric heat capacity and of thermal diffusivity of a polymer, derived at different stages of the experiment (heating in the regime of the third kind and cooling by coolant), provide grounds for calculating thermal conductivity λ, too:

$$\lambda = \frac{P}{\pi\mu_1^2\tau v L}\,\frac{W_{\text{п}}}{W_0}\ln\frac{\Delta l_1}{\Delta l_2}, \tag{17}$$

which obviously follows from equalities (1), (8), and (16).

The accuracy of the dilatometric and thermometric determination of the above-named thermophysical characteristics depends on the accuracy of determination of the values contained in the theoretical formulas. As a rule, the largest error in thermometry does not exceed 4-5%.

However, most of the measured characteristics, in particular the rate of temperature rise in heating and the rate of thermal expansion at this stage, and also the time intervals in cooling and the power used in electric heating, are recorded with an accuracy of up to 1-2%. Therefore, the total error in determining a, β, λ, and c_V does not exceed 6-7%. As was pointed out above, it is particularly important to realize that though the method is suitable for investigating the course of the temperature and the anomalies of the studied thermophysical properties, such investigations were not carried out within the framework of the present article because the object of this work was to describe the theory of the method and partly its instrumental part. As the object to be studied we chose polymethyl methacrylate in the temperature range 30-80°C in which the material is not yet thermolabile (and for which the specialized literature contains data [3] necessary for comparing the obtained results, and consequently taken as reference data).

For the above reason we did not make a special study of thermolabile polymers in the course of the present experiments although the method is also suitable for this kind of investigation.

The following values of the thermophysical characteristics of polymethyl methacrylate were obtained: $a = 1.7 \cdot 10^{-7}$ m^2/sec, $c_V = 840$ kJ/(°K·m^3), $\beta = 62 \cdot 10^{-4}$ °K^{-1}, $\lambda = 2.4$ J/(°K·sec·m); they agree well with the known data [3] on the assumption that the reference temperature is 55°C.

NOTATION

a, thermal diffusivity; λ, thermal conductivity; α, heat-transfer coefficient; β, coefficient of thermal expansion; t, time; τ, time intervals; W, rate of thermal expansion; R, radius of specimen; L, length of specimen; $\Delta l_{I,\ II}$, current elongation of the specimen; ΔL_T, maximum absolute elongation of the specimen; $\Delta l_{1,\ 2}$, increase in length of the specimen within time τ; c_V, heat capacity of the specimen; I_0, Bessel equation of zero order; I_1, Bessel equation of first order; μ_1, first root of the Bessel equation; A, constant; b, parameter; P, power of electric heating; Q, total power of thermal losses; v, rate of change of the temperature; $\Delta T_{I,\ II}$, current values of the temperature.

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DETERMINATION OF THE TEMPERATURE OF PIEZOELECTRIC TRANSDUCERS UPON HARMONIC EXCITATION

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The temperature of a thin piezoceramic shell is determined with a view to the dielectric, mechanical, and piezoelectric losses; a comparison of the results of calculation with the experiment shows that the error does not exceed 15%.

The electrophysical properties of ferroelectric materials used in precision measuring technique, viz., dielectric permeability, polarization, elastic and piezoelectric constants (particularly near phase transitions), depend largely on the temperature.

Energy dissipation and the temperature behavior of dielectrics in an alternating electric field were investigated in [1-4]. In distinction to the solution of the disconnected problem of thermoelectroelasticity for an infinite cylindrical shell [4], the present work submits for a transducer with finite dimensions simpler formulas for calculating the temperature and the heat release.

We examine a cylindrical shell $0 \leqslant s \leqslant s_0$ to whose external surfaces the electric potentials $V = V_0 e^{i\omega t}$ are applied (Fig. 1).

The equations of motion of a cylindrical shell have the form [5]

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