DETERMINATION OF THE THERMOPHYSICAL CHARACTERISTICS OF POLYMERIC COMPOSITES

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A method is described for determining the temperature dependences of thermophysical characteristics from space–time measurements of the temperature fields in the test specimens.

Polymeric composite materials have found broad use as degradable coatings for protection from heat. Classical methods of determining the thermophysical characteristics of such materials in the temperature range above the point at which the materials begin to undergo thermal degradation do not consider the specifics of the processes that are occurring. Methods involving the solution of inverse heat-conduction problems [1-12] are currently widely used to solve problems of this nature.

Below we describe a method of calculating the thermophysical characteristics of degradable thermally protective coatings in the temperature range 300-2300°K. The thermophysical characteristics are calculated by a numerical method on a computer from the experimentally determined temperature field through the thickness of the specimen over time. As the initial equation we took a nonlinear heat-conduction equation with a term which accounts for thermal degradation of the material [13, 14]:

$$c\rho \frac{\partial T}{\partial \tau} = \frac{\partial}{\partial x}\left(\lambda \frac{\partial T}{\partial x}\right) - c_g G_g \frac{\partial T}{\partial x} - \Delta Q. \tag{1}$$

The specimen is in the form of a plate thermally insulated on one side. The boundary and initial conditions of the problem are:

$$T(x, 0) = T_0, \tag{2}$$

$$T(l, \tau) = T_l(\tau), \tag{3}$$

$$\frac{\partial T(0, \tau)}{\partial x} = 0. \tag{4}$$

Allowing that

$$\Delta Q = q_f \frac{d\rho}{d\tau} = q_f \frac{\partial \rho}{\partial T} \frac{\partial T}{\partial \tau}, \tag{5}$$

we write Eq. (1):

$$\frac{1}{a} \frac{\partial T}{\partial \tau} = \frac{\partial^2 T}{\partial x^2} + \frac{1}{\lambda} \frac{\partial \lambda}{\partial T} \left(\frac{\partial T}{\partial x}\right)^2 - k \frac{\partial T}{\partial x}, \tag{6}$$

where

$$a = \frac{\lambda}{c\rho + q_f \lambda \partial \rho / \partial T}; \tag{7}$$

$$k = c_g G_g \Psi(T)/\lambda. \tag{8}$$

The function $\Psi(T)$ is equal to zero outside the temperature range in which thermal degradation takes place, while inside this range it is equal to unity. This corresponds to

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the physical situation in which k is equal to zero and the term $k(\partial T/\partial x)$ in (6) is absent below the temperature at which degradation begins and above the temperature at which it ends.

We introduce the dimensionless quantities:

$$r = \frac{x}{\Delta x}, \quad t = \frac{\tau}{\Delta \tau}, \quad T_{\text{rel}} = \frac{T(x, \tau)}{T_{\text{m}}}.$$

As Δx we can for example take the distance between the two closest thermocouple junctions. As $\Delta \tau$ we can take the time of passage of the isotherm between these junctions, and as T_m we can take the maximum temperature to which the specimen is heated. These parameters can be changed later in the numerical solution of the problem to improve the interpolation and the accuracy of the calculation.

In dimensionless variables, Eq. (6) takes the form:

$$A\frac{\partial T_{\text{rel}}}{\partial t} = \frac{\partial^2 T_{\text{rel}}}{\partial r^2} + L\left(\frac{\partial T_{\text{rel}}}{\partial r}\right)^2 - K\frac{\partial T_{\text{rel}}}{\partial r}, \tag{9}$$

where

$$A = \frac{1}{a}\frac{(\Delta x)^2}{\Delta \tau}; \tag{10}$$

$$L = \frac{1}{\lambda}\frac{\partial \lambda}{\partial T_{\text{rel}}}; \tag{11}$$

$$K = \frac{c_g G_g}{\lambda}\Delta x. \tag{12}$$

In the general case, the coefficients α, λ, and k for polymer composites depend on the temperature and the rate of temperature change over time [10, 14]. Here, we examine a variant in which the dependence of the thermophysical characteristics on heating rate can be ignored.

Thus, the problem is reduced to obtaining the dimensionless unknowns A, L, and K from (9). Knowing them, we can use Eqs. (10), (11), and (12) to determine the sought thermophysical characteristics.

We will represent the solution of Eq. (9) in the form of an expansion in powers of r^n:

$$T_{\text{rel}}(r, t) - T_{\text{rel}}(0, t) = \left.\frac{\partial T_{\text{rel}}}{\partial r}\right|_{r=0} r + \left.\frac{\partial^2 T_{\text{rel}}}{\partial r^2}\right|_{r=0}\frac{r^2}{2!} + \left.\frac{\partial^3 T_{\text{rel}}}{\partial r^3}\right|_{r=0}\frac{r^3}{3!} + \left.\frac{\partial^4 T_{\text{rel}}}{\partial r^4}\right|_{r=0}\frac{r^4}{4!} + \left.\frac{\partial^5 T_{\text{rel}}}{\partial r^5}\right|_{r=0}\frac{r^5}{5!} + \cdots \tag{13}$$

We use Eq. (9) to find expressions for the temperature derivatives with respect to the coordinate up to the sixth order, inclusively, at the point r = 0. We insert these values into (13). Then, after certain transformations, we obtain

$$\frac{1}{A}\Delta T_{\text{rel}}(r, t) = \frac{K}{A}\int_0^r \Delta T_{\text{rel}}(r', t)\,dr' + \frac{\partial}{\partial t}\int_0^r dr'\int_0^{r'} T_{\text{rel}}(r'', t)\,dr'' + \left(\frac{1}{A}\frac{\partial A}{\partial t} - \frac{2L}{A}\frac{\partial^2 T_{\text{rel}}}{\partial r^2}\right)\int_0^r dr'\int_0^{r'}\Delta T_{\text{rel}}(r'', t)\,dr'', \tag{14}$$

where

$$\Delta T_{\text{rel}}(r, t) = T_{\text{rel}}(r, t) - T_{\text{rel}}(0, t). \tag{15}$$

In Eq. (14), all of the coefficients with integrals are taken at the point r = 0. To determine the three unknowns 1/A, K/A and $B = 1/A(\partial A/\partial t - 2L\partial^2 T_{\text{rel}}/\partial r^2)$, it is necessary to measure temperatures at four points r_0, r_1, r_2, and r_3. Finally, the system of three equations for finding the unknown coefficients 1/A, K/A, and B takes the standard form

$$\frac{1}{A}a_{i1} - \frac{K}{A}a_{i2} - Ba_{i3} = b_i \quad (i = 1, 2, 3), \tag{16}$$

where

$$a_{i1} = \Delta T_{\text{rel}}(r_i, t) = T_{\text{rel}}(r_i, t) - T_{\text{rel}}(r_0, t); \tag{17}$$

$$a_{i2} = \int_0^{r_i} \Delta T_{\text{rel}}(r', t)\, dr'; \tag{18}$$

$$a_{i3} = \int_0^{r_i} dr' \int_0^{r'} \Delta T_{\text{rel}}(r'', t)\, dr''; \tag{19}$$

$$b_i = \int_0^{r_i} dr' \int_0^{r'} \frac{dT_{\text{rel}}(r'', t)}{dt}\, dr''. \tag{20}$$

The coefficients a_{ij} and b_i were obtained by approximation of $T_{rel}(r, t)$ with respect to r and t and subsequent integration.

The empirical dependence of T_{rel} on r was approximated with a polynomial of a degree no higher than five, while the empirical dependence of T_{rel} on t was approximated by a third-order spline function.

In the temperature range in which the material does not undergo thermal degradation, Eq. (16) takes the form

$$\frac{1}{A} a_{i1} - B a_{i3} = b_i. \tag{21}$$

To use the proposed method, a unit [15, 16] was designed and made which makes it possible to record temperature–time dependences and thermogravimetric characteristics with a specified heating regime.

The main elements of the unit for determination of thermophysical characteristics are an automatic programmed-heating system, a temperature measurement system, and a high-temperature heating device located in the test chamber and connected to a high-frequency semiconductor transducer.

The thermogravimetric characteristics are determined with the use of a high-temperature test chamber with an automatic programmed-heating system, an analytical balance with a transducer to convert the mechanical displacement of the balance into an electrical signal, and instruments to record the temperature and the change in specimen weight.

To determine the thermophysical characteristics, the copper test chamber (Fig. 1a) includes a copper, water-cooled induction coil 1 installed on a ceramic slab 2 secured to the top plate of the chamber 3 on four rods 4. Lateral heat-insulating ceramic shields 5 and 6 are placed in the coil 1 on the slab 2, which has a centering belt. The heater 7 is in the form of two identical hollow cylinders of high-strength graphite.

To have the test conditions approximate service conditions and to allow for escape of thermal degradation products during heating, fixing elements 10 were installed symmetrically between the specimens and the heater. The fixing elements were corundum rings with an outside diameter of 50 mm and a height of 4 mm and sixteen radial grooves. Another corundum ring 11 with an outside diameter of 50 mm and a height of 10 mm was installed between the specimens 8. The distorting thermal effect of the fixing elements 10 and ring 11 on the specimens 8 was alleviated by having the elements and ring contact the specimens along a line 0.2 mm wide.

The specimens 8 with thermocouples 9, fixing elements 10, ring 11, and heater 7 were installed on the bottom shield 12. The bottom shield is connected to the top shield 13 by means of clamp 14. The thermocouples 9 are brought outside the chamber through special holes in the top plate, while argon is fed into the chamber during testing to provide an inert medium (not indicated in the figure).

Use of the hollow cylindrical heaters, which roughly simulate the radiation of a blackbody, make it possible to obtain a more uniform heat flow to the surface being heated. In-

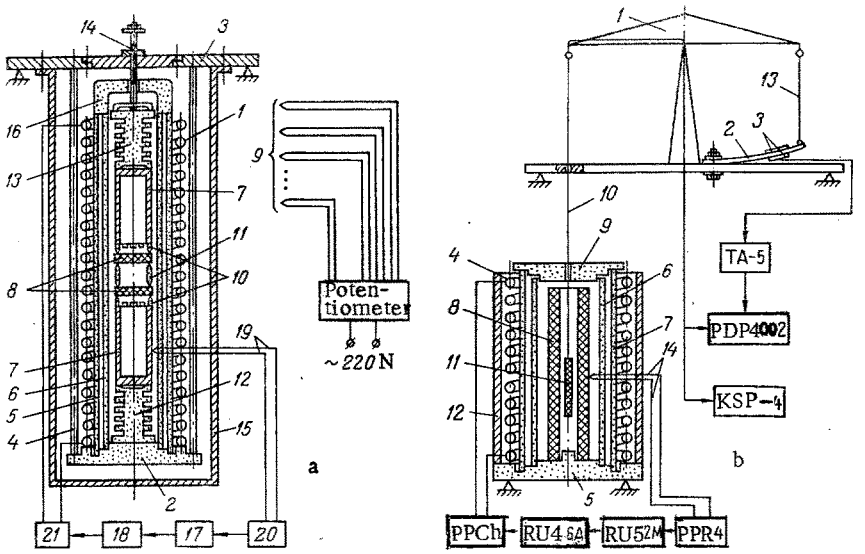

Fig. 1. Basic diagrams of high-temperature testing chamber for determining thermophysical characteristics (a) and for thermogravimetric studies (b).

troduction of the ring 11 between the specimens 8 makes it possible to assume adiabatic conditions on the sides of the specimens facing each other when they are heated symmetrically. This requirement is necessary due to the boundary conditions established for determination of diffusivity and relative thermal conductivity. In the present scheme, the moderate degree of heating asymmetry does not have such a strong effect on the temperature distribution on the sides of the specimens facing each other due to their slight effect on each other.

The chamber is surrounded outside by a ferrite shield 15, while a corundum shield 16 is installed above on side shields 5 and 6. The controlled heating system consists of an electronic program-control and setting device 17 and an automatic control device 18 to control the thermocouple 19 installed on the heater 7 and connected with a potentiometer 20. The heating system also includes high-frequency semiconductor transducer 21, which is connected with the copper water-cooled coil 1.

The water-cooled induction coil 1, powered from the high-frequency 65 kW, 10 kHz semiconductor transducer 21 heats the symmetrically positioned elements of the graphite heater 7 in accordance with the prescribed program when the transducer is turned on. The automatic programmed heating system uses devices 17, 18, and 20 to change the output power of the transducer 21. The energy radiated by the heater 7 increases the temperature of the surface of the specimen 8 turned toward it at a prescribed rate. The specimens have the form of circular plates 50 mm in diameter and 4 mm thick. Each contains rolled-in thermocouple junctions located at different distances through the thickness and installed during manufacture. The coordinates of the junctions are refined after plate manufacture by taking x-ray photographs of the specimens.

The measurements during the experiment reduced to recording the temperature at specified points of the specimen over time. Dual information was obtained from one test. The symmetry of the heating was monitored with a KSP-4 electronic automatic potentiometer. Chromel–alumel thermocouples were used to measure temperatures up to 1400°K, while tungsten–rhenium thermocouples were used up to 2100°K.

Figure 1b shows a basic diagram of the unit for determining the thermogravimetric characteristics. It includes an analytical balance 1, a transducer 2 to convert the mechanical displacements of the balance into an electrical signal and consisting of an elastic element 2 with strain gauges 3 stuck onto it, and a water-cooled copper induction coil located on a ceramic slab 5. Ceramic heat-insulating shields 6 and 7 and a cylindrical radiant heater 8 are located inside the coil 4 on the ceramic slab 5. The hole in the heater is closed from above by another ceramic shield 9 made of two parts and having an opening for the thermocouple 10. The specimen 11 of polymeric composite material measuring 15 × 60 mm and up to 1 mm in thickness is suspended on the thermocouple 10.

To ensure an inert medium during the tests, the chamber is filled with argon (not indicated in the figure). The outside of the coil 4 is surrounded by a ferrite shield 12. The thermocouple 10 is secured to one side of the balance beam 1. One end of the elastic element 2 is attached to the other side of the beam by a thin steel wire 13, while the other end of the element is attached directly to the base of the balance 1. The automatic programmed heating system consists of a block which includes RU5-02M, RU4-16A, and PPR-4 instruments and a thermocouple 14. The system functions through changes in the output power of the high-frequency semiconductor transducer FST. The temperature and weight loss in the unit are recorded with a PDP4-002 two-coordinate potentiometer, a KSP-4 automatic electronic potentiometer, and a TA-5 tensometric amplifier.

The water-cooled induction coil 4, connected with the high-frequency transducer FST, heats the cylindrical radiant heater 8 in accordance with the specified program when the transducer is turned on. The heater, radiating thermal energy, raises the temperature of the specimen 11 at a prescribed rate. The change in the weight of the specimen 11 during heating changes the deflection of the elastic element 2. The latter change is detected by strain gauges 3 which lead through the TA-5 amplifier to one of the channels of the PDP4-002 potentiometer. A signal is sent from the Chromel–Alumel thermocouple 10 to the other channel of the PDP4-002 potentiometer and to the KSP-4 automatic potentiometer. The PDP4-002 potentiometer records the change in specimen weight as a function of temperature, while the KSP-4 potentiometer records the change in specimen temperature over time.

When necessary, the above unit can heat the specimen to 3300°K, since the upper temperature boundary is determined by the melting point of the radiant heater — which is made of heat-resistant graphite. The specimen temperature can be determined in this case with standard photoelectric pyrometers.

Thus, the unit for determining thermogravimetric characteristics makes it possible to determine the temperatures of the beginning and end of thermal degradation with the same heating regimes as in the unit for determining the thermophysical characteristics. The temperatures at the beginning and end of degradation depend on the heating rate and go into the mathematical model. It is therefore important to know these characteristics for specified heating regimes.

The unit was used to determine temperature–time relations and thermogravimetric characteristics of several grades of glass-fiber-reinforced plastics in a specific regime of monotonic heating. The relations found for a and $\bar{\lambda}$ agreed well with the data obtained for these materials in the temperature range up to the beginning of thermal degradation on the unit described in [17].

NOTATION

x, coordinate; T, temperature; τ, time; ρ, density; c, specific heat of the test material; λ, thermal conductivity of the test material; $\bar{\lambda}$, relative thermal conductivity of the test material; c_g, specific heat of the volatile products of thermal degradation; G_f, flow of volatile thermal-degradation products; ΔQ, thermal effect from physicochemical transformations; q_f, heat flux; l, thickness of specimen (plate); a, diffusivity of test material; r, dimensionless coordinate; t, dimensionless time; T_{rel}, dimensionless temperature; r', r'', relative running coordinates; $n = 0, 1, 2, \ldots$, exponent. Indices: $i = 1, 2, 3$; $j = 1, 2, 3$.

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