CALCULATION OF HEAT CONDUCTION IN POLYMER MATERIALS DURING THERMAL DEGRADATION

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An analysis is made of the process of heat conduction during heating of bodies made of materials subject to thermal degradation. An example is given of the calculation and its experimental verification for the specific test conditions applicable to heating of a plate of glass-reinforced plastic.

The occurrence of thermal degradation in heat-sensitive polymer building materials, accompanied by absorption of heat and copious emission of gas, promotes increased thermal stability during strong heating. This property of polymers is widely used in technology to create different kinds of heat-protective coatings. As regards the nature of the processes involved, heating of polymers above the temperature at which thermal degradation begins corresponds in many ways to drying of moist materials. This permits the calculation of temperature distribution in heat shield layers by the methods of drying theory [1].

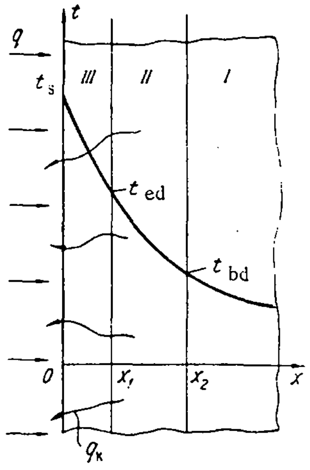

Fig. 1. Temperature distribution in the surface layers of polymer material when heated above the temperature at which thermal degradation begins.

Let us examine the condition of surface layers of a plate of polymer material when heat is supplied to one of its sides; we shall distinguish three zones in the heated plate, depending on the temperature (Fig. 1). In the zone of temperatures not greater than that at which thermal degradation begins (zone 1), heat conduction is described by the equation

$$c\gamma\frac{\partial t}{\partial\tau}=\frac{\partial}{\partial x}\left(\lambda\frac{\partial t}{\partial x}\right),\quad x>x_2.$$

Endothermic decomposition of the polymer occurs in zone 2, accompanied by gasification. The gaseous products of thermal decomposition migrate toward the heated surface, moving along the pores that are formed. Heat and mass conduction in the second zone may be described by the system of equations:

$$c\gamma\frac{\partial t}{\partial\tau}=\frac{\partial}{\partial x}\left(\lambda\frac{\partial t}{\partial x}\right)-\frac{\partial}{\partial x}(c_2t_2q')+Q_{cr}\frac{\partial\gamma}{\partial\tau},$$

$$\frac{\partial\gamma_2}{\partial\tau}=\frac{\partial}{\partial x}q'+\frac{\partial\gamma}{\partial\tau};\ x_1<x<x_2. \tag{1}$$

The thermophysical coefficients in (1) depend on temperature and heating rate, since the process of vaporization, which determines the thermal conductivity and other thermophysical properties of the material being decomposed, proceeds in time.

In zone 3, adjacent to the plate surface, the thermal degradation process terminates, and therefore the volume heat sources cease to act. The heat and mass transfer equations in this zone have the form

$$c\gamma\frac{\partial t}{\partial\tau}=\frac{\partial}{\partial x}\left(\lambda\frac{\partial t}{\partial x}\right)-\frac{\partial}{\partial x}(c_2t_2q'),$$

$$\frac{\partial\gamma_2}{\partial\tau}=\frac{\partial}{\partial x}q';\quad 0<x<x_1.$$

The boundary conditions on the contact surfaces between neighboring zones are as follows:

$$\text{when } x=x_2\quad t_1(x,\tau)=t_2(x,\tau),\ q_1'(x,\tau)=q_2'(x,\tau),$$

$$\lambda_1\frac{dt_1}{dx}=\lambda_2\frac{dt_2}{dx},$$

$$\text{when } x=x_1\quad t_2=t_3,\ q_2'(x,\tau)=q_3'(x,\tau),\ \lambda_2\frac{dt_2}{dx}=\lambda_3\frac{dt_3}{dx}.$$

To solve the composite equations we make use of a numerical method [2], with the aid of which we will determine the temperature distribution in a glass-reinforced textolite plate based of ED-6 resin.

The conditions of the problem are: a plate 8 mm thick with initial temperature 20° C identical over the whole thickness of the plate is heated from one side by means of a liquid which satisfies the condition Bi → → ∞. Thus a constant temperature of 600° C is established on the plate surface. The opposite surface of the plate is thermally insulated. It is required to determine the temperature field in the plate 40 sec after the start of heating. The thermophysical properties of the given plastic in the range 20–600° C were determined experimentally by the author at various rates of temperature increase by Barskii's method [3, 4] and were presented in [5, 6] (Fig. 2).

We shall simplify the equations of heat and mass transfer as applied to the given heating conditions. For epoxy resin the temperature at which thermal degradation ceases is roughly 600° C, and there is therefore no third zone in the given case. We note further that during experimental determination of heat capacity, thermal decomposition took place in the course of heating of the polymer, and the values of heat capacity found, determined in this way, take into account the thermal effects of the chemical reactions. This permits us to combine the first and subsequent terms of the heat conduction equation when solving (1), using the apparent (effective) value of heat capacity with allowance for the chemical reactions.

Finally, as analysis shows, a substantial simplification of this problem may be derived from the fact that the effects accompanying gas flow along the channels prove to have only a slight influence on the heat conduction process can be neglected in the calculaion. Allowing for these simplifications, and also making the usual assumptions of drying theory, it may be considered that

$$c_{\text{eff}}\gamma\frac{\partial t}{\partial\tau}=\frac{\partial}{\partial x}\left(\lambda\frac{\partial t}{\partial x}\right)+ + c_2 q'\frac{\partial t}{\partial x}\cdot \tag{2}$$

The loss of accuracy in replacing (1) by (2) does not exceed the experimental error in determining the thermophysical properties.

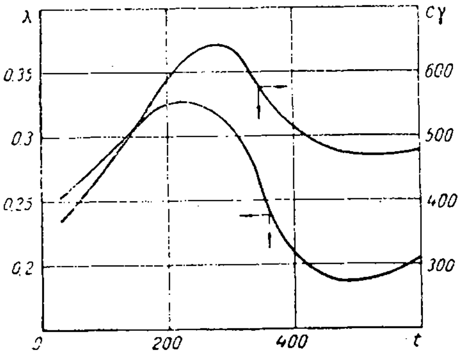

Fig. 2. Dependence of the thermophysical properties λ, kcal/m · hr · degree, and cγ, kcal/m³, of glass-reinforced textolite on temperature t, °C.

We shall solve the problem by a numerical method. To this end we replace the continuous temperature distribution by a stepwise one, derived from temperature values determined from the formula

$$t_{i,k+1}=t_{i,k}+\left[\lambda\left(\frac{t_{i,k}+t_{i+1,k}}{2}\right)(t_{i+1}-t_{i,k})-\lambda\left(\frac{t_{i,k}+t_{i-1,k}}{2}\right)(t_i-t_{i-1})-q_2' C_2(t_{i+1,k}-t_{i,k})\,\Delta x\right](\Delta x^2 C_{\text{eff}\,i,k}\gamma_{i,k})^{-1}\Delta\tau. \tag{3}$$

Formula (3) may be simplified, using the Osid-Yushkov [2] elementary balance method, which is based on use of the auxiliary function

$$G(t)=\int\lambda(t)\,dt.$$

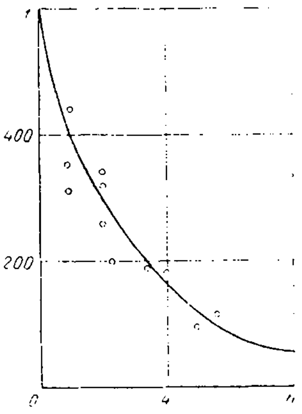

Fig. 3. Distribution of temperature, t, °C in a plate of glass-reinforced textolite (h in mm).

In this case the solution may be written in finite differences as

$$t_{i,k+1}=t_{i,k}+[G_{i-1,k}-2G_{i,k}+G_{i+1,k}+ - q' c_2(t_{x+\Delta x}-t_x)](\Delta x^2 c_{\text{eff}\,i,k}\gamma_{i,k})^{-1}.$$

We shall assume that the condition for convergence of the solution is the same as for the solution without account for the term expressing the convective component of the heat flux:

$$\Delta\tau\leqslant c(t)_{\min}\gamma(t)_{\min}\Delta x^2/2\lambda(t)_{\max}$$

for all values of t, since the presence of this term leads to reduction of the heat fluxes (for given heating conditions) and smooths out fluctuations of the numerical solution.

The equation for the flux density of the products of thermal decomposition may be written in finite differences as follows:

$$\Delta q'=\frac{\Delta\gamma}{\Delta t}\,\frac{\Delta t}{\Delta\tau}\,\Delta x+\varepsilon', \tag{4}$$

where ε' reduces to a quantity as small as desired when the partition intervals $\Delta\tau$ and Δx are reduced. For convenience of carrying out the calculation, (4) may be written as follows:

$$\Delta q_i'=\frac{\gamma(t_{i+1,k})-\gamma(t_{i,k})}{t_{i+1,k}-t_{i,k}}\,\frac{t_{i+1}-t_{i,k}}{\Delta\tau}\,\Delta x. \tag{5}$$

The quantity $\Delta q_i'$ is determined with the aid of (5) from the graphs of thermal decomposition kinetics $\gamma = \gamma(t)$ as a function of heating rate [6].

The mass flux density at an arbitrary section is determined from the formula

$$q_i'=\sum_{1}^{k}\Delta q_i'. \tag{6}$$

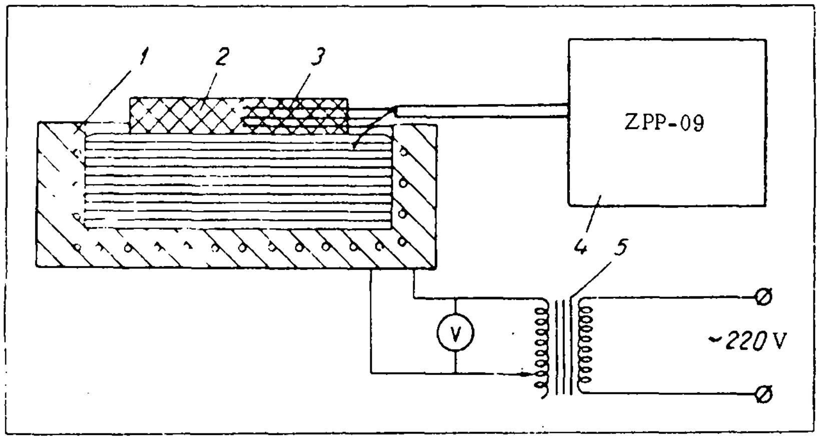

Fig. 4. Schematic of the instrument for experimental verification of the calculated heat conduction process: 1) body of tray with fused metal; 2) specimen; 3) thermocouples; 4) recorder; 5) variable voltage supply to instrument.

The values q_i' obtained according to (6) are substituted in (3).

In carrying out calculations with account for variation of the thermophysical properties with heating rate for each time interval, it is necessary to find the derivative of temperature with respect to time. The existence of limiting values of the thermophysical properties with regard to heating rate (or, as is assumed in the terminology of molecular physics, the existence of "instantaneous values of the thermophysical constants" [7]) facilitates the calculation of the heat conduction process. As the calculation shows, for given conditions the values of heating rate are sufficiently large for the limiting values of the thermophysical properties of the material [5] to be used. In Fig. 3 the temperature distribution is presented for a plate, calculated according to (3). The figure shows also experimental points obtained in heating a specimen of glass-reinforced textolite of given size with the aid of fused tin in a special dish (Fig. 4). The coefficient of heat transfer from the metal to the specimen, determined from Mikheev's formula, was $\alpha = 2220$ kcal/m^2 · hr · degree (Bi = 355). Thus we may take the surface temperature to be 600° C with a high degree of accuracy (the error does not exceed 4° C).

NOTATION

c, γ, λ—coefficients depending on temperature; c_2, t_2, γ_2—heat capacity, temperature, and specific weight of gas; Q_{cr}—heat of chemical reaction of thermal decomposition; q'—gas mass flow density; $t_{i,k}$—temperature in i-th layer at time k; ε'—error in converting to finite differences; t_s—surface temperature; t_{bd}—temperature at beginning of decomposition; t_{ed}—temperature at end of decomposition; q—heat flux supplied; q_c—convective component of heat flux at plate.

REFERENCES

1. A. V. Luikov, Heat and Mass Transfer in Drying Processes [in Russian], Gosenergoizdat, 1956.

2. P. P. Yushkov, Trudy instituta energetika AN BSSR, no. 10, 1959.

3. A. F. Kapustinskii and Yu. P. Barskii, Izvestiya sektora F. Kh. A. IONKh, vol. 20, 1950.

4. Yu. P. Barskii, Trudy NII stroikeramiki, no. 8 [in Russian], Promstroizdat, 1953.

5. O. F. Shlenskii, Yu. P. Barskii, and N. P. Pichugin, Plastmassy, no. 1, 1964.

6. O. F. Shlenskii, Plastmassy, no. 10, 1964.

7. I. G. Mikhailov, V. A. Solos'ev, and Yu. P. Syrnikov, Fundamentals of Molecular Acoustics [in Russian], Izd. "Nauka," 1964.

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