HEAT AND MASS TRANSFER IN VITROPLASTICS

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Mathematical models of heat transmission in oriented vitroplastics are analyzed and methods of determining the parameters of these models are described.

Reinforced plastics constitute heterogeneous systems consisting of two basic components (a polymer binder and a filler) with markedly different thermophysical properties and of not the same physicochemical stability, which makes their behavior during heating rather complex. Depending on the temperature level, the transmission of heat in these materials is affected by different physicochemical processes occurring in each and the heating process alone will be described by different systems of equations. In this study the author will analyze, referring to [1], the mathematical models of the heat transmission process in oriented vitroplastics and will discuss problems in the determination of the parameters of these models.

1. Within the range of moderate temperatures, where neither of the two basic components undergoes chemical changes, heat is transmitted through a vitroplastic by conduction only, and the process can be described by the equation of anisotropic heat conduction for a continuous medium with certain effective thermophysical properties which depend on the overall material structure as well as on the volume content and the properties of the components:

$$c\rho \frac{\partial T}{\partial t} = \frac{\partial}{\partial x}\left(\lambda_{xx}\frac{\partial T}{\partial x}\right) + \frac{\partial}{\partial y}\left(\lambda_{yy}\frac{\partial T}{\partial y}\right) + \ldots + \frac{\partial}{\partial z}\left(\lambda_{zy}\frac{\partial T}{\partial y}\right). \tag{1}$$

When determining the effective properties, we will consider the vitroplastic to consist of two basic components: glass fiber and polymer binder, with gaseous inclusion present either as a byproduct of technological process or deliberately injected into the material:

$$n_{\mathrm{g}} + n_{\mathrm{p}} + m_0 = 1. \tag{2}$$

The density and the specific heat of a vitroplastic are, by virtue of being scalar quantities, determined by the simple weighted sum of their respective values for the basic components (the contribution of the gaseous phase is very small and, therefore, disregarded):

$$\rho = n_{\mathrm{g}}\rho_{\mathrm{g}} + n_{\mathrm{p}}\rho_{\mathrm{p}}, \tag{3}$$

$$c = \frac{1}{\rho}(n_{\mathrm{g}}\rho_{\mathrm{g}}c_{\mathrm{g}} + n_{\mathrm{p}}\rho_{\mathrm{p}}c_{\mathrm{p}}). \tag{4}$$

In order to determine the thermal conductivity, one must know the material structure (the distribution of its components). We will, therefore, first consider an individual unidirectionally reinforced layer of vitroplastic. The thermal conductivity in the direction of the reinforcement is also determined by the sum of two terms: the thermal conductivity of the glass fiber and that of the porous binder:

$$\lambda^{\parallel} = \lambda n + \bar{\lambda}_{\mathrm{p}}(1 - n_{\mathrm{g}}). \tag{5}$$

The quantity $\bar{\lambda}_p$ can be calculated according to Odolevskii's formula [2] with the thermal conductivity of a monolithic binder and the porosity $m_p = m_0/(1-n_g)$.

For the thermal conductivity in a plane perpendicular to the reinforcing fibers, with the random distribution and the mutual orientation of these fibers taken into account, we have the following approximation formula:

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$$\lambda^{\perp} = \frac{\bar{\lambda}_{p}}{1-n_{g}\left(1-\frac{\bar{\lambda}_{p}}{\lambda_{g}}\right)-0{,}045\left(\frac{\lambda_{g}}{\bar{\lambda}_{p}}-1\right)^{\frac{1}{2}}(1-0{,}42\,|n_{g}-0{,}4|)(1+57\sigma^{2}n_{g}^{2/3}}, \qquad (6)$$

which has been very accurate (maximum error ±3%) within the ranges of parameters $0.2 \leq n_g \leq 0.7$ and $1 \leq \lambda_g/\lambda_p \leq 10$. It has been assumed in the calculations that the fibers are circular in cross section, that structurally the material consists of squares and hexagonal unit cells arrayed at random and oriented arbitrarily, and that the occurrence of both types of cell structures is equiprobable, with the volume content of the reinforcement material distributed normally [3]. The effective thermal conductivity of the unit cells was calculated from the results of numerical solutions to respective heat conduction problems.

For a sheet of vitroplastic whose thickness is δ and which consists of n layers with equal contents but different orientations of glass fibers, the components of the thermal conductivity tensor are defined as follows:

$$\begin{gathered}
\lambda_{xx} = \lambda^{\perp} + (\lambda^{\parallel} - \lambda^{\perp}) \sum_{j=1}^{n} \frac{\delta_j}{\delta} \cos^2\theta_j, \\
\lambda_{yy} = \lambda^{\parallel} - (\lambda^{\parallel} - \lambda^{\perp}) \sum_{j=1}^{n} \frac{\delta_j}{\delta} \cos^2\theta_j, \\
\lambda_{xy} = \lambda_{yx} = \frac{1}{2} (\lambda^{\parallel} - \lambda^{\perp}) \sum_{j=1}^{n} \frac{\delta_j}{\delta} \sin 2\theta_j, \\
\lambda_{zz} = \lambda^{\perp}, \quad \lambda_{xz} = \lambda_{zx} = \lambda_{yz} = \lambda_{zy} = 0,
\end{gathered} \qquad (7)$$

where θ_j denotes the angle between the fiber orientation in the j-th layer and the Ox axis.

2. A thermal breakdown of the binder, which occurs when a vitroplastic is heated to high temperatures, causes significant changes in the heat transmission process. Chemical reactions during the breakdown are accompanied by thermal effects which cause a redistribution of heat sources and heat sinks in the material, the power of those being determined by the decomposition process. The gaseous products generated by such a decomposition begin to flow through the simultaneously forming pores and, as a result, heat is now transmitted through the material also by convection. The change in the chemical composition as well as the formation of pores in the binder have the effect of altering the thermophysical properties of the material.

The system of equations describing the heat transmission through reinforced plastics during the decomposition of the binder must, if the said effects are taken into account, include an equation of chemical kinetics in the decomposition process, equations of mass, energy, and momentum conservation, and also an equation of state for the gaseous phase.

The thermal breakdown of polymers is a complex multistage process which, according to the theory of complex chemical reactions, can be described by an overall kinetic equation. This kinetic equation must refer to the equilibrium state, which for polymers is characterized by a thermogravimetric decomposition curve $\rho_{tg}(T)$ representing the variation in polymer density as a function of the temperature during isothermal heating. Such a thermogravimetric curve is shown in Fig. 1 for phenolformaldehyde resol.

The Arrhenius equation of kinetics, generalized on the basis of the $\rho_{tg}(T)$ relation, will be written as

$$\frac{\partial \rho_p}{\partial t} = \begin{cases} -B\rho_{p0}\left(\frac{\rho_p - \rho_{tg}(T)}{\rho_{p0}}\right)^n \exp\left(-\frac{\Delta E}{RT}\right) & \text{at } \rho_p > \rho_{tg}(T), \\ 0 & \text{at } \rho_p \leqslant \rho_{tg}(T), \end{cases} \qquad (8)$$

where B, n, and ΔE are universal kinetic parameters of the process (reaction rate coefficient, reaction order, and activation energy, respectively) generally depending on the temperature and on the extent of binder decomposition $\eta = (\rho_{p0} - \rho_p)/(\rho_{p0} - \rho_{pc})$.

Assuming that the solid and the gas are at the same temperature at every point in the body, we can determine the quasisteady gas flow and the drag on the basis of Zhukovskii's hypothesis

$$\vec{R}_d = -m\,\frac{\mu_G(T)}{K}\,s\vec{V},$$

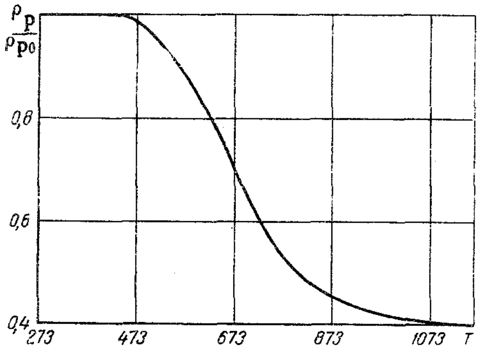

Fig. 1

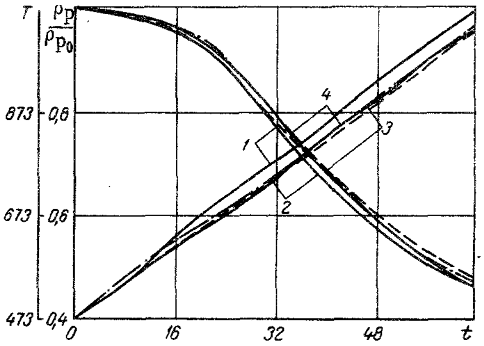

Fig. 2

Fig. 1. Thermogravimetric curve of phenolformaldehyde resol binder decomposition.

Fig. 2. Variation in the density of phenolformaldehyde resol binder during heating at the rate dT/dt = 10 deg/sec (numbers refer to respective tests): time t (sec); temperature T (°K).

and, disregarding the kinetic energy of the gaseous phase as well as the work of pressure and friction forces along with a few other terms whose effect on the thermal state of the material is negligible, we obtain the following equations of energy, mass, and momentum conservation:

$$c(T,\ \eta)\rho\,\frac{\partial T}{\partial t}=\operatorname{div}\left(\lambda(T,\eta)\operatorname{grad}T\right)-\operatorname{div}(\rho_G s\vec{V}c_G T)-\Delta H(T,\ \eta)\,n_p\frac{\partial\rho_p}{\partial t},\tag{9}$$

$$\operatorname{div}(\rho_G\, s\vec{V})+n_p\frac{\partial\rho_p}{\partial t}=0,\tag{10}$$

$$\operatorname{grad}(\xi p)+m\,\frac{\mu_G(T)}{K}\,s\vec{V}=0,\tag{11}$$

where

$$\rho=\rho_0-n_p\eta\,(\rho_{p0}-\rho_{pc});$$

$$m=m_0+n_p\,\frac{\rho_{p0}-\rho_p}{\rho_{p0}}.$$

The system is closed by the equation of state for the gaseous phase

$$p=\frac{R}{M_G}\,\xi\rho_G T.\tag{12}$$

System (8)-(12), with given initial and boundary conditions for a given shape of the body, determines the temperature field, the binder burnout, the pressure, the density, and the mass flow rate of the decomposition products in the material.

In the one-dimensional case with an impermeable cold surface, system (8)-(12) splits into two systems of equations:

$$\left.\begin{aligned}
&c(T,\ \eta)\rho\,\frac{\partial T}{\partial t}=\frac{\partial}{\partial z}\left(\lambda(T,\ \eta)\,\frac{\partial T}{\partial z}\right)-\frac{\partial}{\partial z}(\rho_G sVc_G T)-\Delta Hn_p\frac{\partial\rho_p}{\partial t},\\
&\frac{\partial\rho_p}{\partial t}=\begin{cases}-B\rho_{p_0}\left(\dfrac{\rho_p-\rho_{tg}}{\rho_{p_0}}\right)^n\exp\left(-\dfrac{\Delta E}{RT}\right) & \text{at}\ \ \rho_p>\rho_{tg}(T),\\ 0 & \text{at}\ \ \rho_p\leqslant\rho_{tg}(T),\end{cases}\\
&\frac{\partial}{\partial z}(\rho_G sV)+n_p\frac{\partial\rho_p}{\partial t}=0,
\end{aligned}\right\}\tag{13}$$

$$\left.\begin{aligned}
&\frac{\partial}{\partial z}(\xi p)+m\frac{\mu_G}{K}\,sV=0,\\
&p=\frac{R}{M_G}\,\xi\rho_G T,
\end{aligned}\right\}\tag{14}$$

of which the first one is independent and describes the thermal state of the material, while the second one determines the hydrodynamic parameters p and ρ_G but depends on the solution to the first one.

3. In order to apply the system of equations to practical cases, it is necessary to know the values of its coefficients representing the parameters of the material. Some of these parameters (for example, λ and c at moderate temperatures) are either known, or can be found by known methods based on an experimental study of processes under conditions where the describing equations have solutions in closed form, and a subsequent extrapolation of the thus obtained parameter values to other process modes and conditions. The determination of other process parameters requires new methods based on tests pertaining to the process under arbitrary (and thus also actual operating) conditions and a subsequent solution of reverse problems.

Taking into account these requirements, precisely, methods have been developed for determining the kinetic parameters of the thermal breakdown process in polymer binders and for determining the thermophysical properties of a vitroplastic heated to high temperatures.

The method of determining the thermal breakdown parameters is based on the use of test data pertaining to weight changes in thin ($\delta < 0.5$ mm) vitroplastic specimens during transient heating. If the temperature function is known and if Eq. (8) is assumed to describe the thermal breakdown of the binder, then the theoretical weight change in a specimen can be calculated and, consequently, the problem becomes one of determining the kinetic parameters B, n, and ΔE on the basis of the most accurate correlation between the established $\omega(t)$ function and the test curve $\omega_e(t)$.

With the standard deviation as the measure of the proximity between the calculated and the tested $\omega(t)$ relation, and with the results of K experiments under various conditions considered here so as to eliminate random measurement errors and to cover the entire range of process modes, we obtain the following equation:

$$\Delta=\left\{\frac{1}{K}\sum_{k=1}^{K}\frac{1}{\bar{t}_k}\int_{0}^{\bar{t}_k}\left[\omega_k^{(e)}(t)-\omega(t)\right]^2 dt\right\}^{\frac{1}{2}}=\min, \tag{15}$$

the solution to which, within limits based on thermochemical considerations

$$B(\eta)>0,\quad n(T,\ \eta)>0,\quad \Delta E(T,\ \eta)>0 \tag{16}$$

will determine the sought kinetic parameters B, n, and ΔE.

The existence of limits (16) and the nonlinearity of functional (15) make the search for minimizing the functions $B(\eta)$, $n(T, \eta)$, and $\Delta E(T, \eta)$ difficult. Expressing the functions in the form of series will make the task easier, reducing it to a minimization of functional (15) with respect to a finite number of parameters (series coefficients). The search for the minimum is conducted by the method of steepest descents [4] with a subsequent increase in the number of parameters, and is terminated as soon as the value of Δ either lies within the error limits of measured data (weight of a specimen) or ceases to decrease with succeeding approximations (with added series terms).

In accordance with this procedure, the author has experimented with the thermal breakdown of phenolformaldehyde resol binder (Fig. 2). The tests were performed with a special-purpose high-sensitive thermobalance at heating rates of 1, 3, 5, and 10 deg/sec (a total of 15 tests).

In determining the kinetic parameters it was assumed that B = exp (b) and that

$$b=\sum_{h}a_h\eta^h;\quad n=\text{const};\quad \Delta E=\sum_{p}d_p\frac{1}{T^p}. \tag{17}$$

The order of the approximating polynomials was taken successively equal to h = p = 0, 1, 2, 3. The calculations were made on a model M-20 digital computer. As a result, the following expressions were obtained for the kinetic parameters with p = h = 1:

$$B=\exp(15.5-5.1\,\eta)\frac{1}{\text{sec}};\quad n=0.81;\quad \frac{\Delta E}{R}=\left(19430-\frac{48.4\cdot 10^5}{T}\right)\text{°K}. \tag{18}$$

The standard deviation of $\omega(t)$ values calculated from the test data was 2% for the entire test series; the maximum standard deviation in a single test was 3.1%. A further refinement of these expressions is not

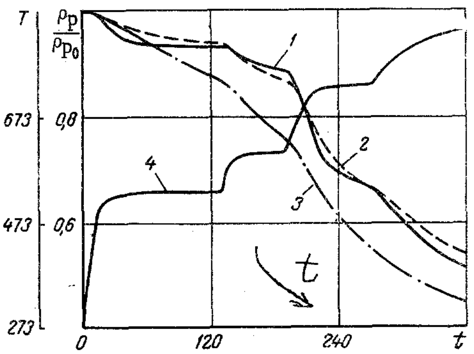

Fig. 3

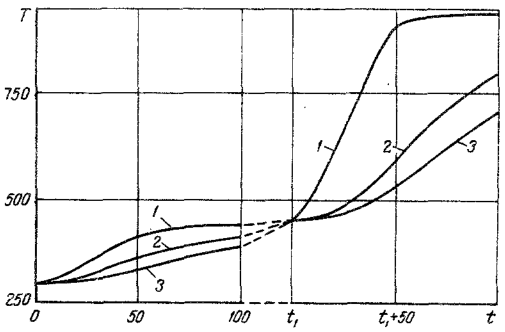

Fig. 4

Fig. 3. Variation in the density of phenolformaldehyde resol binder during stepwise heating: 1) test curve; 2) curve according to Eq. (8); 3) calculation with ρ_{tg}(T) disregarded; 4) temperature–time curve (t, sec; T, °K).

Fig. 4. Heating modes: 1) temperature of heated specimen surface; 2) temperature at the center of the specimen; 3) temperature of copper plate. Temperature T (°K); time t (sec).

worthwhile and would be inappropriate, inasmuch as the attained accuracy of data fitting is within the accuracy limits of measurements and introducing higher-order approximating polynomials will not improve it significantly ($\Delta = 1.929$ with $p = h = 2$). Such a close agreement between calculated and measured values leads one to the conclusion that the proposed description of thermal breakdown in polymer binders does correctly reflect the laws governing that process. Additional confirmation is provided by the results of compound heating tests (Fig. 3).

The methodology of determining the thermophysical properties of vitroplastics is based on the use of test data pertaining to temperature variations across the specimen thickness during transient heating. The temperature readings at the surfaces serve as the boundary conditions, while the temperatures at internal points are used for calculating the minimizing quadratic functional of differences between calculated and measured temperatures at these points. The differences are calculated relative to the temperature level, by solving the equation of heat conduction or the system of Eqs. (13). The thermophysical properties as functions of the material state variables are sought in terms of appropriate series. This procedure is very practical, because it requires no special mathematical tools and makes the experimental analysis much simpler, also because – and this is most important – it makes feasible the determination of these characteristics while chemical reactions occur in the material and conventional methods of analysis fail.

In accordance with this procedure, the specific heat and the thermal conductivity perpendicular to reinforcing fibers were determined for the grade AG-4S vitroplastic. Since for a unique solution of the problem with a simultaneous determination of $\lambda^{\perp}$ and c are needed additional conditions, hence the measurements were made on flat specimens, each with a calorimetering copper plate bonded by means of a heat resistant adhesive to the surface opposite the heated one. These specimens were now heated by thermal radiation in such manner as to make the surface temperature vary linearly first up to 453°K and then, after letting the heat distribute over the entire specimen, up to 953°K (Fig. 4).

A combined evaluation of four experiments has yielded for the 273–453°K temperature range

$$\lambda^{\perp} = 0.515\ \text{W/m}\cdot\text{deg}, \qquad c = 985\ \text{J/kg}\cdot\text{deg},$$

with a standard deviation $\Delta = 2.3$°K. These values are close to the averages obtained for this temperature range by conventional methods.

Within the 453–953°K temperature range, when thermal breakdown of the binder occurs, we have

$$\lambda^{\perp} = 0.515\,[1 + 0.0006\,(T - 453)]\,(1 - 0.39\eta)\ \text{W/m}\cdot\text{deg},$$

$$c = 985\,[1 + 0.0014\,(T - 453) - 0.1\,\eta]\ \text{J/kg}\cdot\text{deg},$$

with $\Delta = 20°\text{K}$. These $\lambda^{\perp}(T, \eta)$ and $c(T, \eta)$ relations conform to known physical concepts.

The thermal conductivity parallel to reinforcing fibers $\lambda^{\parallel}$ can be determined by the same method; this was not done here because of the unavailability of specimens.

NOTATION

x, y, z	are the space coordinates;
t	is the time;
ρ	is the density;
ρ_{pc}	is the density of coke residue;
ρ_{tg}	is the thermogravimetric density of polymer;
c	is the specific heat;
λ	is the thermal conductivity;
$\bar{\lambda}_p$	is the thermal conductivity of porous polymer;
$\lambda^{\parallel}$	is the thermal conductivity parallel to reinforcing fibers;
$\lambda^{\perp}$	is the thermal conductivity in a plane perpendicular to reinforcing fibers;
p	is the pressure;
n_g, n_p	are the volume content of glass fiber and of polymer binder, respectively;
m	is the porosity;
s	is the clearance;
θ	is the angle;
δ	is the thickness;
σ	is the parameter of the distribution law;
B	is the reaction rate coefficient;
n	is the reaction order;
R	is the universal gas constant;
ρ_G	is the density of gas;
ΔH	is the thermal effect;
M	is the molecular weight;
η	is the extent of decomposition;
R_d	is the drag force;
V	is the velocity;
K	is the gas permeability;
g	is the acceleration of gravity;
μ	is the dynamic viscosity;
ω	is the weight;
$\bar{t}$	is the duration (time) of test.

Subscripts

p	denotes the polymer;
g	denotes the glass fiber;
G	denotes the gas;
0	denotes the initial condition.

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