DURATION OF THE VISCOFLUID STATE OF THERMOSETTING PLASTICS UNDER ARBITRARY HEATING CONDITIONS

Zh. P. Terent'eva and M. L. Fridman

UDC 678.067

A method for estimating the duration of the viscofluid state of a thermosetting material under nonisothermal heating during injection molding is developed on the basis of the generalized Arrhenius equation.

A thermoplastic is injection-molded while it in a viscofluid state. Since all the stages in actual injection molding press occur under obviously nonisothermal conditions, the classical Arrhenius equation

$$\tau = A \exp\left\{\frac{\Delta U}{RT}\right\}, \tag{1}$$

which holds only for isothermal conditions, is insufficient for determining the duration of the viscofluid state of the thermoplastic. In the viscofluid state all the fractions of the resins in a thermosetting plastic gradually pass from one curing stage to another. As a result, at various stages of processing thermosetting plastics are put into deep stages of polycondensation. The choice of optimal processing conditions thus requires a method for determining the duration of the viscofluid state as a function of the initial properties of the material under isothermal conditions and as a function of variable plasticization conditions (time and temperature) in the process of filling a mold to make the product.

We shall develop such a method by estimating the duration of the viscofluid state of thermosetting plastics under arbitrary heating conditions and times from the relation [1]:

$$A = \int_0^{\tau} \exp\left\{-\frac{\Delta U}{RT(x, y, z, t)}\right\} dt. \tag{2}$$

Equation (2) is a unique relation between the independent state parameter A, which characterizes the amount of products in the composition that can react, and the duration τ of the viscofluid state during which the temperature of the polymer can vary arbitrarily. When the temperature is constant in time, i.e., when $\partial T/\partial t = 0$, Eq. (2) goes over into the Arrhenius equation (1).

The numerical value of A and the activation energy ΔU of the polycondensation reaction can be obtained from the Arrhenius equation on the basis of isothermal viscometric experiments at different temperatures T_1 and T_2 with the corresponding values τ_1 and τ_2 of the duration of the viscofluid state at these temperatures, viz.,

$$\Delta U = \frac{R \ln(\tau_1/\tau_2)}{1/T_1 - 1/T_2}, \tag{3}$$

$$A = \tau_1 \exp\left\{-\frac{\Delta U}{RT_1}\right\}. \tag{4}$$

We note here that the activation energy ΔU, as established on the basis of special viscometric tests [1], is virtually independent of the polycondensation stage and retains a constant value for each specific material throughout the entire viscofluid state.

If the injection molding process is arbitrarily divided into stages, characterized by their own temperatures and times, Eq. (2) becomes

$$A = \sum_{i=1}^{n} \int_0^{\tau_i} \exp\left\{-\frac{\Delta U}{RT_i(t)}\right\} dt, \tag{5}$$

G. S. Petrov Scientific-Research Institute of Plastics, Moscow. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 58, No. 2, pp. 250-254, February, 1990. Original article submitted July 14, 1988.

where τ_1 and $T_1(t)$ are the period of time and the time-dependent distribution of the polymer temperature for each stage. In particular, for three stages τ_1 and $\tau_1(t)$ are the time and temperature of the viscofluid state of the thermosetting plastic during plasticization in the cylinder of an injection-molding machine, τ_2 and T_2 — during injection, and τ_3 and T_3 — during curing in the mold.

The simplest solution of Eq. (5) is obtained if we ignore transient heating of the material as the thermal conditions change from stage to stage and if we assume that the temperature remains constant during each stage. For this case the duration of the viscofluid state of the material in the mold at a given temperature will be defined as

$$\tau_{\mathrm{m}} = A_n \exp\left\{\frac{\Delta U}{RT_{\mathrm{m}}}\right\}, \tag{6}$$

where

$$A_n = A - \sum_{i=1}^{n-1} \tau_i \exp\left\{-\frac{\Delta U}{RT_i}\right\}. \tag{7}$$

In Eq. (6), which formally coincides with the Arrhenius equation (1), parameter A_n takes into account how the duration of the viscofluid state of a thermosetting plastic in the mold is affected by the previous heating conditions (temperature and time) of the material during plasticization and injection. This effect can be calculated from Eq. (7) or can be estimated empirically by means of the following tests and calculations.

The properties of a thermosetting plastic are determined as a function of the plasticization parameters (the cylinder temperature, rotation frequency of the screw, plasticization, etc.). When these parameters are varied the amount of products in the composition that are capable of reacting changes. All of these changes are reflected in parameter A_n, which is determined from Eq. (7). In order to find this parameter experimentally, upon completion of the plasticization a batch of the material, which is not ready for molding, is injected through the cylinder of the nozzle and is cooled rapidly. The solidified material is turned into powder, which is then studied in a plastometer. From the experimental data (plastometric tests) we calculate the value of parameter A_n, which is characterized by the number of products of the composition that are still capable of reacting. Parameter $A_n(T, f, p, \ldots)$, so determined as a function of the plasticization parameters, can be used with Eq. (6) to also determine the time for which the polymer in the injection mold will be in a viscofluid state at the given mold-wall temperature T_m. The resulting information can be the basis for choosing the more productive and technologically effective means of processing the thermosetting plastic.

In the general case, for a particular distribution of the temperature field $T = T(x, y, z, t)$ the time $\tau(x, y, z)$ marking the end of the viscofluid state at any point in the polymer can be determined from Eq. (2). The unknown duration of the viscofluid state, however, is the upper limit of the integral and Eq. (2) does not have an exact analytical solution. The solution of Eq. (2) will be sought by approximate methods. In our analysis of the filling of the mold we make the following assumptions: a tapped flow is realized, the slip velocities are low, and the heat release due to viscous flow is negligible; the material is heated because of pure heat conduction and convective heat transfer is disregarded; the heat released at the wall because of sliding friction is carried off into the body of the mold, whose wall temperature is kept constant at T_m; the temperature T_0 is distributed uniformly in the polymer melt as it enters the mold; the duration of the viscofluid state of the thermosetting material at T_0 is longer than that at T_m, i.e.,

$$\tau_0/\tau_{\mathrm{m}} = \exp\left\{\frac{\Delta U}{R}\left(\frac{1}{T_0} - \frac{1}{T_{\mathrm{m}}}\right)\right\} > 1.$$

Assuming that the material is heated from temperature T_0 at each point of the melt to the the temperature of the mold wall before the viscofluid state of the polymer at the given point ends, i.e.,

$$\tau_{\mathrm{m}}(x, y, z) \geqslant t_{\mathrm{m}}(x, y, z), \tag{8}$$

we simplify the initial equation (2) with allowance for the assumptions made above and we obtain

TABLE 1. Duration of Viscofluid Stateof K-18-24 Phenoplast in a Field of Variable Temperature Over the Cross Section of the Sample

$x/h\,(y=0)$	0	0,2	0,4	0,6	0,8	1,0
$y/l\,(x=0)$	0	0,2	0,4	0,6	0,8	1,0
τ_m, sec	43,15	42,14	39,8	34,6	26,2	13,8

$$\tau_m(x,\ y,\ z)=t_m(x,\ y,\ z)+ + \exp\left\{\frac{\Delta U}{RT_m}\right\}\left(A_n-\int_0^t \exp\left\{-\frac{\Delta U}{RT(x,\ y,\ z,\ t)}\right\}dt\right). \tag{9}$$

From Eq. (9) we can determine the duration of the viscofluid state $\tau_m(x, y, z)$ of the polymer at each point of the mold for particular properties (characterized by parameter A_n) of the material entering the material. The transient distributions of the temperature T(x, y, z) and time $t_m(x, y, z)$ when heating the polymer to the temperature T_m of the mold wall are calculated. The parameter A_n can be estimated from Eq. (7) or empirically using the procedure as altered above during variation of the plasticization parameters and choice of the optimal plasticization temperature and time, preceding the stage of molding the products. The integral on the right side of Eq. (9) does not have an exact analytical solution for an arbitrary temperature field distribution. It can be calculated by approximate methods. To do so we use the method parabolas (Simpson's method) [2], dividing the region of integration with equal steps into n parts in the general case. Confining the discussion to three dividing points (0, $t_m/2$, t_m) and replacing the integral in Eq. (9) with its approximate value, we finally obtain

$$\tau_m(x,\ y,\ z)=A_n\exp\left\{\frac{\Delta U}{RT_m}\right\}+t_m\left[\frac{5}{6}-\frac{1}{6}\exp\left\{\frac{\Delta U}{R\theta_1}\right\}-\frac{2}{3}\exp\left\{\frac{\Delta U}{R\theta_2}\right\}\right]. \tag{10}$$

Thus, to determine the duration of the viscofluid state of a polymer at any point (x, y, z) during filling of an injection mold with wall temperature T_m it is sufficient to know the time required to heat the polymer at that point to T_m and the value of the temperature $T(x, y, z, t_m/2)$, which is established at that point in half the time of heating the material to T_m. These data can be determined from the known solutions of the heat equation, which are presented fully in the monograph by Lykov [3]. For practical applications it is also convenient to use approximate analytical solutions of the heat equation [4].

Table 1 gives the calculated durations of the viscofluid state during the molding of K-18-24 phenoplast in the form of a bar measuring 2h × 2ℓ (2h = 0.5 cm, 2ℓ = 2.0 cm) with initial temperature T_0 = 120°C and mold-wall temperature T_m = 170°C. The coordinate system is fixed to the center of the bar. The properties of K-18-24 phenoplast are: thermal diffusivity $a = 0.5 \cdot 10^{-3}$ m^2/h, ΔU = 22.4 kcal/mole, and $A_n = 1.13 \cdot 10^{-10}$ sec.

The calculated values of the duration of the viscofluid state of a thermosetting plastic in an injection mold when the material is heated nonisothermally are in satisfactory agreement with the experimental data on the processing of the given material and are the determining factor in the choice of the curing time in the mold.

NOTATION

x, y, and z, spatial coordinates; T, absolute temperature; T_0, temperature of the polymer as it enters the mold; T_m, temperature of the injection mold; τ, duration of the viscofluid state; t_m, time required to heat the polymer to the mold-wall temperature; ΔU, polycondensation activation energy; f, rotation frequency of the screw of the injection machine; p, plasticization pressure; A and A_n, parameters characterizing the amount of products in the composition that are capable of reacting, for the initial thermosetting plastic and with allowance for the history of the effect of the temperature and time on the polymer; R = 8.314 J/mole·deg, gas constant; and $\theta_1 = T_m T_0/(T_m - T_0)$ and $\theta_2 = T_m(x, y, x, t_m/2)/T_m - T(x, y, z, t_m/2)$, dimensionless temperature complexes. Subscripts: m indicates the respective quantities when the temperature of the injection mold is reached; i labels the quantities in the stages of the processing; and n is the number of stages.

LITERATURE CITED

1. A. I. Leonov, N. I. Basov, and Yu. V. Kazankov, Fundamentals of Injection Molding of Thermosetting Plastics and Rubbers [in Russian], Moscow (1972).
2. R. V. Hemming, Numerical Methods [Russian translation], Moscow (1972).
3. A. Y. Lykov, Heat Conduction Theory [in Russian], Moscow (1967).
4. M. Bio, Variational Principles in Heat Exchange Theory [in Russian], Moscow (1977).

METHOD FOR MEASUREMENT OF RADIATION, TRANSMISSION, AND REFLECTION COEFFICIENTS OF SEMITRANSPARENT MATERIALS

G. K. Kholopov and V. I. Kopysov

UDC 535.23

Basic principles and results of testing a technique for determining the radiation properties of materials are presented.

Solution of many problems in thermophysics and applied optics requires reliable information on the radiation properties of materials. The basic source of such information is experimental studies. In connection with this, measurement of radiation, transmission, and reflection coefficients of transparent and diffusely transmitting materials — crystals, glasses, plastics, films, tissues, grids, etc — is of special interest. Measurement of radiation coefficients of such materials involves the greatest methodological difficulties.

As a rule the known methods and apparatus for measurement of radiation coefficients of semitransparent materials at both high [1, 2] and moderate and low [3, 4] temperatures are based on comparison of the radiation from the specimen under study with that of a reference source — a black body. One of the major requirements is then the need for uniform heating (or cooling) of the specimen and equality of its temperature to that of the black body. This complicates technical realizations of the measurement apparatus and (or) leads to significant errors in measurement.

The technique to be described below realizes a new method of measuring radiation, transmission, and reflection coefficients of semitransparent materials in the infrared (IR) range of the spectrum [5], which does not require equalization of the temperatures of the specimen studied and the reference radiation source, but requires only the constancy of both those temperatures over the period of the measurement cycle.

A diagram of equipment realizing this method and explaining its basic principles is shown in Fig. 1. Two black bodies 1 and 2 are mounted by a rotation device 3 in chamber 4 with isothermal nontransparent walls. A uniform wall temperature is achieved, for example, by bathing the walls with a heat exchange agent supplied by tubes from a temperature-stabilized volume. The temperatures of the black bodies differ and are maintained stable, for

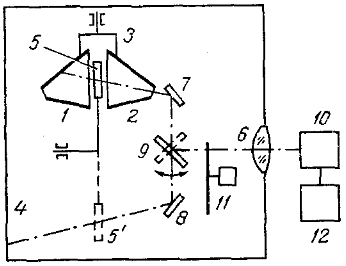

Fig. 1. Diagram of device for realization of measurement method.

Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 58, No. 2, pp. 254-260, February, 1990. Original article submitted September 26, 1988.