

NONISOTHERMAL FLOW OF A MOLTEN POLYMER  
 ACCOMPANIED BY A FIRST-ORDER PHASE TRANSITION

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A theoretical discussion is presented for the filling of a mold by a melt of crystalline polymer; the theoretical relationships agree well with the experimental ones.

In pressure dye casting of polymers, the material is forced into the mold and sets there. The scope for exact adoption of the mold shape is important, because it is obvious that the flow is very much non-isothermal, and hence the filled length of the cavity remains finite.

One cannot use the relationships derived for nonisothermal flow on the assumption that the thermo-physical properties are independent of temperature [1, 2] because thermoplastics such as polyolefins and polyamides, which are typical crystalline polymers, do not behave in this way (Fig. 1). These materials show a marked change in thermal diffusivity (Fig. 1b) over a narrow temperature range called the crystallization region, which indicates that in this range there is a phase transition very similar in nature to a first-order phase transition.

We therefore consider the flow of a molten crystalline polymer (Fig. 2) having an initial temperature  $T_0$  and a pressure  $P_0$  at the inlet to the mold, whose wall temperature is  $T_w$ ; we then distinguish the region of mobile liquid core, temperature  $T_1(x, y, t)$ , from the region of solidified material at the wall, temperature  $T_2(x, y, t)$ . The interface has coordinate  $y_0$ , which is dependent on time, and has a characteristic temperature  $T_*$  for the crystallization region. In the casting of such polymers we have

$$(T_* - T_w) \gg (T_0 - T_*).$$

We take as one-dimensional the flow in the cavity between two unbounded parallel plates having a separation  $2h$ , apart from a region at the inlet (region  $a$ ) and at the flow front itself  $l(t)$  (region  $b$ ), both of which have lengths very small compared with those of the casting generally. This is a fairly crude mode of calculation, but we shall see that it gives satisfactory quantitative agreement between theory and experiment.

In fact, the thickness of the solidified layer varies along the length of the component.

The length of the cast component is comparatively great, so this scheme involves the assumption that a section through the thickness presents in adjacent parts layer thicknesses that vary to a negligible extent.

The liquid core continues to move and the cast length continues to increase until the mobile interfaces meet (the condition  $y_0 = 0$ ). If the polymer in the mold is incompressible, and the density is independent of temperature, the equation of motion for the quasistationary state takes the form

$$\partial P / \partial x = \partial \tau_{y,x} / \partial y. \quad (1)$$

We take the power law form for the equation describing the deformation of the liquid core:

$$dV/dy = \tau^n_{y,x} / \eta(T) \quad \text{for } n > 1, \quad (2)$$

where the  $\eta(T)$  relationship takes the form

$$\eta = \eta_0 \exp\left(\frac{b}{T_0 - T_*}\right), \quad (3)$$

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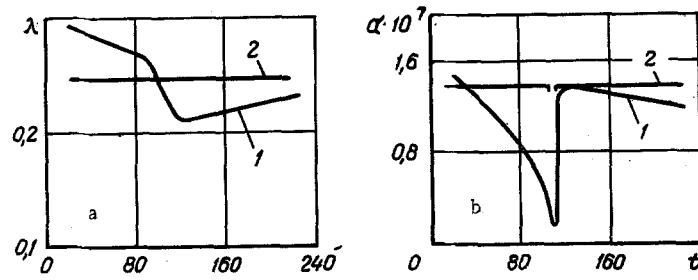


Fig. 1. Temperature dependence of: a) thermal conductivity; b) thermal diffusivity for low-density polyethylene [3]: 1) true curve; 2) approximation used in solving thermal problem ( $\lambda$ , W/m·deg;  $\alpha$ , m<sup>2</sup>/sec, t, °C).

and we substitute (2) into (1) and integrate twice with the following boundary conditions

$$\left. \frac{dV}{dy} \right|_{y=0} = 0, \quad V|_{y=y_0(t,x)} = 0, \quad (4)$$

and introduce the mean-flow speed

$$\bar{V} = \frac{dl}{dt} = \frac{1}{y_0} \int_0^{y_0(t,x)} V(y,t) dy, \quad (5)$$

to get the expression

$$\frac{dl}{dt} = \left( \frac{dP}{dx} \right)^n \frac{1}{y_0(t,x)} \int_0^{y_0(t,x)} y^{n+1} [\eta(T)]^{-1} dy. \quad (6)$$

Then we have to derive  $y_0(t, x)$  and  $T(y, x, t)$  from the energy equations for the region of solidified polymer and the liquid core.

The following assumptions are made in solving the thermal part of the problem. The thermal diffusivity  $\alpha$  of the melt is equal to that of the solidified material and is independent of temperature (curve 2 of Fig. 1b), and the crystallization region is localized at temperature  $T_*$ , where  $\alpha(T)$  shows a discontinuity, and there is an interface between the phases, which arises because there is a definite latent heat of fusion  $r$ . We also assume that the thermal conductivity  $\lambda$  of the melt is equal to that of the solidified polymer.

We neglect dissipative heat production in the liquid core.

The temperature gradient in the  $x$  direction is much less than that in the  $y$  direction, since equal finite temperature differences  $T_0 - T_*$  are attained in the first case in lengths that are larger by 1-2 orders of magnitude than those in the second, so we assume that

$$\partial T_1 / \partial x = 0. \quad (7)$$

A consequence of assumption (7) is that there is no convective heat transfer in a liquid core, and hence that  $T_1$ ,  $T_2$ ,  $y_0$ , and  $\partial P / \partial x$  are independent of  $x$ ; the latter in (6) may then be replaced by

$$(T_* - T_w) \gg (T_0 - T_*).$$

The differential equations for thermal conduction then take the following form:

$$\frac{\partial T_1}{\partial t} = \alpha \frac{\partial^2 T_1}{\partial y^2}; \quad 0 < y < y_0(t), \quad (8)$$

$$\frac{\partial T_2}{\partial t} = \alpha \frac{\partial^2 T_2}{\partial y^2}; \quad y_0(t) < y < h \quad (9)$$

with the following boundary and initial conditions:

$$\left. \frac{\partial T_1}{\partial y} \right|_{y=0} = 0, \quad T_1|_{y=y_0(t)} = T_*, \quad T_1|_{t=0} = T_0, \quad (10)$$

$$T_2|_{y=h} = T_*, \quad T_2|_{y=y_0(t)} = T_*, \quad T_2|_{t=0} = T_0. \quad (11)$$

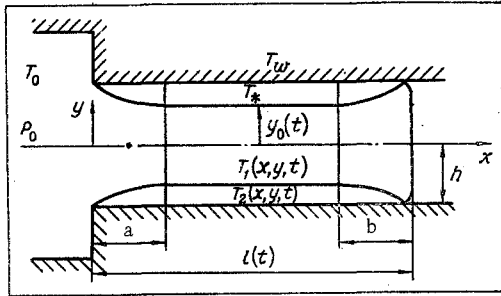


Fig. 2

Fig. 2. Filling of a mold by a crystalline polymer.

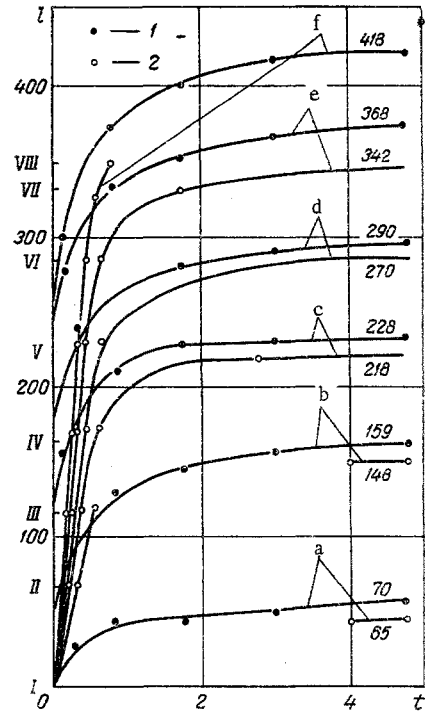


Fig. 3

Fig. 3. Mold filling length as a function of time for various temperatures; component thickness 2 mm. Pressure at outlet to mold 600 kg/cm<sup>2</sup> ( $l$ , mm;  $t$ , sec). Temperatures (°C): a) 180; b) 190; c) 200; d) 210; e) 230; f) 250; 1) calculated curve; 2) experiment. The Roman numerals are the numbers of the transducers placed along the cavity (350 mm from inlet to end). The numbers on the curves are the specimen lengths in mm.

The interface has coordinate  $y_0(t)$ , where the heat flux to the wall is equal to the sum of the flux produced by crystallization and the flux drawn from the liquid core, but the latter can be neglected by virtue of the condition  $(T_* - T_W) \gg (T_0 - T_*)$ ; the final condition at the interface takes the form:

$$\lambda \left. \frac{\partial T_2}{\partial y} \right|_{y=y_0(t)} = r\rho \frac{dy_0(t)}{dt}, \quad (12)$$

where  $\lambda$  and  $\rho$  are the thermal conductivity and density of the polymer respectively.

The  $y_0(t)$  relationship is determined by solution of (9) and (12) together; we introduce the new variable

$$z = \frac{h-y}{2\sqrt{t}}, \quad (13)$$

which has the range of variation

$$0|_{y=h} \leq z \leq z_0|_{y=y_0(t)}, \quad (14)$$

whereupon (9) and (12) take the form

$$-2z \frac{dT_2}{dz} = \alpha \frac{d^2T_2}{dz^2}, \quad (15)$$

$$\left. \frac{dT_2}{dz} \right|_{z=z_0} = \frac{2r\rho}{\lambda} z_0. \quad (16)$$

The solution to (15) subject to the boundary conditions corresponding to (11) takes the form

$$\frac{T_2 - T_W}{T_* - T_W} = \frac{\Phi(z/\sqrt{\alpha})}{\Phi(z_0/\sqrt{\alpha})}, \quad (17)$$

where  $\Phi$  is the error integral,

$$\Phi(z) = \frac{2}{\sqrt{\pi\alpha}} \int_0^{z/\sqrt{\alpha}} \exp\left(-\frac{z^2}{\alpha}\right) dz. \quad (18)$$

We get the following equation by substituting into (17) for  $dT_2/dz$  at  $z = z_0$  and substitution into (16):

$$\frac{\exp(-z_0^2/\alpha)}{z_0\Phi(z_0/\sqrt{\alpha})} = 2\sqrt{\pi} \frac{\alpha r \rho}{\lambda(T_* - T_w)}, \quad (19)$$

from which we determine  $z_0$ . Then in calculating  $z_0$ , we use (13) to derive  $y_0(t)$ .

The relationship  $T_1(y, t)$  is determined by solving (8); we integrate the latter with respect to  $y$  from 0 to  $y_0$  subject to  $\partial T_1/\partial y|_{y=0} = 0$  and get

$$\int_0^{y_0} \frac{\partial T_1}{\partial t} dy = \alpha \frac{\partial T_1}{\partial y} \Big|_{y_0(t)}, \quad (20)$$

and the solution to (20) we seek in the form

$$T_1 = T_* - \varphi(t) \left[ 1 - \frac{y^2}{y_0^2(t)} \right]. \quad (21)$$

Then (21) satisfies the conditions

$$\frac{\partial T_1}{\partial y} \Big|_{y=0} = 0; \quad T_1|_{y=y_0(t)} = T_*.$$

The condition  $T_1|_{t=0} = T_0$  is met only at  $y = 0$  for

$$\varphi(t)|_{t=0} = T_0 - T_*, \quad (22)$$

which is considered sufficient in solving the present problem.

We substitute (21) into (20) and integrate to get

$$y_0\varphi' + \varphi y_0' + 3\alpha\varphi y_0^{-1} = 0$$

or

$$(\varphi y_0)' + 3\alpha y_0^{-2}(\varphi y_0) = 0. \quad (23)$$

Integration of (23) gives

$$\varphi y_0 = C \exp \left[ -3\alpha \int_0^t \frac{dt}{y_0^2} \right], \quad (24)$$

where the constant of integration is defined from the condition  $y_0(t)|_{t=0} = h$ , see (13) and (22):

$$C = (T_0 - T_*)h. \quad (25)$$

Then finally we get for  $\varphi(t)$  by substitution into (24) of values for  $y_0(t)$  and  $T$  followed by integration:

$$\varphi(t) = (T_0 - T_*) (1 - 2z_0\sqrt{t}/h)^{-\left(\frac{3\alpha}{2z_0^2} + 1\right)} \exp \left[ -\frac{3\alpha}{2z_0^2} \cdot \frac{2z_0\sqrt{t}/h}{1 - 2z_0\sqrt{t}/h} \right]. \quad (26)$$

Then  $T_1(y, t)$  is as follows on substituting (26) into (21):

$$\frac{T_1 - T_*}{T_0 - T_*} = \left[ 1 - \frac{y^2}{(1 - \alpha^2)h^2} \right] (1 - \alpha)^{-(\kappa+1)} \exp\left(-\frac{\kappa\alpha}{1 - \alpha}\right), \quad (27)$$

where  $\alpha = 2z_0\sqrt{t}/h$ ;  $\kappa = 3\alpha/2z_0^2$ .

We substitute for  $y_0(t)$  and  $T_1(y, t)$  in (6) and replace the derivative  $\partial P/\partial x$  by  $P_0/l(t)$ , and then introduce the dimensionless variable  $y/y_0 = \xi$  and integrate with respect to  $t$  to get

$$l(t)^{n+1} = \frac{(n+1)P_0^n}{\eta_0} \cdot \frac{h^{n+3}}{2z_0^2} \int_0^{2z_0\sqrt{t}/h} (1 - \alpha)^{n+1} d\alpha \int_0^1 \xi^{n+1} \exp\left[-\frac{b}{T_0 - T_*}\right] \times \frac{\exp[\kappa\alpha/(1 - \alpha)](1 - \alpha)^{\kappa+1}}{(1 - \xi^2)} d\xi, \quad (28)$$

which enables us to follow the filling of the mold. If we substitute into the upper limit in the outer integral in (28) the time corresponding to the end of the filling (condition  $y_0 = 0$ ), which is deduced from (13), we get the expression for the maximal cast length as

$$L = \frac{(n+1)P_0^n h^{n+3}}{\eta_0 2z_0^2} \int_0^1 \int_0^1 [\xi(1 - \alpha)^{n+1}] \exp\left[-\frac{b(1 - \alpha)^{\kappa+1} \exp[\kappa\alpha(1 - \alpha)]}{(T_0 - T_*)(1 - \xi^2)}\right] d\xi d\alpha. \quad (29)$$

Equation (29) relates the maximum possible length of the casting to the rheological quantities  $\eta_0$ ,  $T_*$ ,  $n$ ,  $b$  and the thermophysical ones  $\lambda$ ,  $r$ , and  $\alpha$ , as well as to the technological parameters  $P_0$  and  $T_0$  and the mold geometry  $h$ ; it enables one to estimate the scope for making such components not only in designing molds but also in determining technological working conditions for existing equipment.

Equations (28) and (29) have been checked by casting polypropylene of grade PP-2 under pressure.

The mold in the casting machine was a plate  $20 \times 350$  mm of variable thicknesses: 1, 1.5, 2, and 4 mm. Detectors of strain-gauge type were placed at various points along the length of the mold to record the instant when the front passed a given point (see [4] for the method of measuring the pressure and filling time). The signals from the detectors were recorded by an oscilloscope during filling and thus gave  $l(t)$  for various values of  $P_0$ ,  $T_0$ , and  $h$ . The final cast lengths  $L$  were measured to 1 mm. To derive  $l(t)$  and  $L$  to correspond with experimental values we used (28) and (29) to determine  $T_*$  by a thermomechanical method, while the thermophysical characteristics  $\alpha$  and  $r$  were determined in the steady thermal state, and the rheological constants  $n$ ,  $\eta_0$ ,  $T_*$ , and  $b$  were determined by capillary viscometry. The computations from (28) and (29) were performed with a BESM-4 computer.

Figure 3 compares the calculated and observed  $l(t)$  and  $L$ , and the discrepancies in  $l(t)$  are considerable (up to 25%) only during the initial stage of filling, which has little influence on the discrepancy between the calculated and observed  $L$  (maximum cast length 350 mm), the error in the latter case not exceeding 5%.

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