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SUMMARY

Crystallized layer growth from a hot polymer melt on a cold metal surface is treated theoretically. The classical solution of the boundary value problem for "heat diffusion controlled" growth is replaced by a (numerical) solution of the more adequate boundary value problem for "nucleation rate controlled" growth. In this way the unrealistic square root dependence of the layer thickness on time, possessing an infinite initial slope, is replaced by a dependence with finite initial slope, which furnishes the experimentally relevant growth speed at the temperature of the cold wall. The importance of this new approach for the description of the processes occurring in the material during the quench on a cold wall is stressed.

INTRODUCTION

In the course of experimental activities aiming at the determination of the speed of crystallized layer growth from a sheared polymer melt (1) (2) (3) the authors got engaged into the problems of a correct theoretical treatment of their findings. As the crystallized layer initially grew linearly with respect to the time elapsing from the moment of contact with the cold surface, the classical treatment had to be ruled out immediately, since this treatment results in the prediction of an infinite initial growth speed (4). After all, it seems very surprising to the present authors that, so far, nobody has discussed this shortcoming, to say nothing of the omission to propose a more adequate treatment of the problem (5) (6).

In this connection, however, it should be mentioned that the discrepancy between the results of classical treatment and experimental findings has first been observed with swelling experiments (7). As is well known, the basic equations for mass and heat transfer are of identical structure. However, since it was observed that swelling of the polymer was only possible after something like a phase transition had taken place, the boundary value problem is different from ours. An adequate solution was given recently (8). Translated into our situation this would mean that the temperature of the polymer melt should stay at its original value until the crystallization front arrives. In reality, however, this temperature does not remain constant but goes down at least until the melting point is reached. It even decreases much farther until, finally, the supercooled melt starts crystallizing at a finite speed, which is a unique function of temperature (9). The pertinent treatment will now be outlined.

THE BOUNDARY VALUE PROBLEM

The geometry envisaged is that of two parallel and infinitely extended plates with the polymer filling the interstitial space. Before the experiment is started, both plates are thought to be at a temperature T_i well above the thermodynamic melting point T_m of the polymer. At time zero one of these plates is thought to be suddenly cooled to a temperature T_w well below the thermodynamic melting point of the polymer. In order to achieve the growth of a smooth layer with a sharp demarcation with respect to the melt, one has to introduce a shearing. Mentally this can be accomplished by the introduction of a constant speed of one plate with respect to the other. As is well known, the amount of shearing is of great influence on the speed of crystal growth (10) (1) (2) (3). Mathematically, however, this flow condition does not enter as a convection term into our problem, since the plates are thought to be infinitely extended.

The following dimensionless variables are introduced:

$$x^* = x/D \quad , \quad t^* = t\, a_f/D^2, \; \Theta = (T-T_w)/(T_i-T_w)$$

$$\gamma = a_f/a_c \; , \quad \varepsilon = \lambda_f/\lambda_c \quad , \; \Lambda = H/\left[c\;(T_i-T_w)\right] \qquad \ldots(1)$$

where x is the distance from the cold plate, D is the fixed distance between the plates (density changes by the solidification being ignored), T is the temperature, a_f and a_c are the heat diffusivities of the fluid and of the crystal, respectively, λ_f and λ_c are the corresponding heat conductivities, H is the latent heat of crystallization and c is the heat capacity of the crystal, t^* being the Fourier number.

With these variables the equation of conduction of heat reads for the pertinent phases:

$$\partial\Theta/\partial t^* = (1/\gamma)\;\partial^2\Theta/\partial x^{*2} \qquad \text{(crystal)}$$

$$\partial\Theta/\partial t^* = \partial^2\Theta/\partial x^{*2} \qquad \text{(fluid)} \qquad \ldots(2)$$

The initial condition is $\Theta(0,x^*) = 1$, whereas the four boundary conditions read:

$$\Theta(t^*,0) = 0 \quad \ldots(a), \qquad \Theta(t^*,1) = 1 \quad \ldots(b)$$

$$\partial\Theta/\partial x^*|_c = \varepsilon\partial\Theta/\partial x^*|_f + \gamma\,\Lambda\;dx_c^*/dt^* \qquad \ldots(c)$$

$$\Theta_c(t^*,\,x_c^*(t^*)) = \Theta_f\;(t^*,\,x_c^*(t^*)) \qquad \ldots(d) \qquad \ldots(3)$$

By eq. (3c) the heat balance at the moving boundary is expressed, x_c^* being the distance of this boundary from the cold wall. By eq. (3d) the continuity of the temperature at this boundary is postulated (physical equilibrium).

In the classical treatment (4) (11) boundary condition

(3d) is tightened by the postulate that $\Theta_c = \Theta_f$ must be equal to Θ_m = const. (thermodynamic equilibrium). In avoiding overdetermination, in boundary condition (3c) one has to give dx_c^*/dt^* free. In this way the layer growth becomes "diffusion rate controlled". Putting $x_c^* \propto \sqrt{t^*}$ one obtains the well known analytical Neumann solution (11) (for penetration into half infinite space). According to this solution the polymer melt must show the ability to crystallize at arbitrarily increasing rates when zero time is approached. For this reason the Neumann solution must be discarded.

Alternatively, however, one can avoid to predetermine the value of $\Theta_c = \Theta_f$ and consider it as the solution of the problem. According to this procedure one has to introduce a growth speed dx_c^*/dt^*, as determined by experiment, into boundary condition (3c). In this way this growth speed is accepted as being "nucleation rate controlled". The mathematical problem becomes now much more complicated, since dx_c^*/dt^* is a function of the crystallization temperature, which, on its part, depends on t^* and $x_c^*(t^*)$:

$$dx_c^*/dt^* = \phi(\Theta(t^*, x_c^*(t^*))) \qquad \ldots(4)$$

This problem has been solved numerically, using appropriate data for polypropylene (γ = 0,54; ε = 0,60; Λ = 0,9 (with $T_i - T_w$ = 155°C)) and a parabolic approximation for the function $\phi(\Theta)$ of eq. (4), possessing a maximum ϕ_m = 0,52 (T_w = 90°C) and going through zero at the melting point T_m and at the glass-transition temperature T_g(160°C and 60°C respectively). This ϕ_m is derived from the highest growth speed observed so far by us on polypropylene under shear. For Λ, also several other values, including zero, were chosen in order to show that this parameter has practically no influence at small Fourier numbers t^*. In our case of D = 1 mm t^* = 1 corresponds (for polypropylene) to t = 11,63 s, which is a rather long time, if injection moulding is envisaged. In Figs. 1 to 4 the obtained results are shown.

CONCLUSIONS

Details of this calculation will be published elsewhere. The fact that the reduced latent heat Λ is of minor influence at low Fourier numbers opens the way for approximate analytical solutions in the range of Fourier numbers relevant to injection moulding. From Fig. 1 we learn that the initial slope, which gives the layer growth speed at the temperature of the wall, must be readily accessible to an experimental determination. In fact, the curves do not show pronounced curvatures at t^* = 0. From Figs. 1 and 2 we learn that the approach of the steady state is considerably retarded. This is due to the fact that the crystallization speed goes to zero when the melting point is reached.

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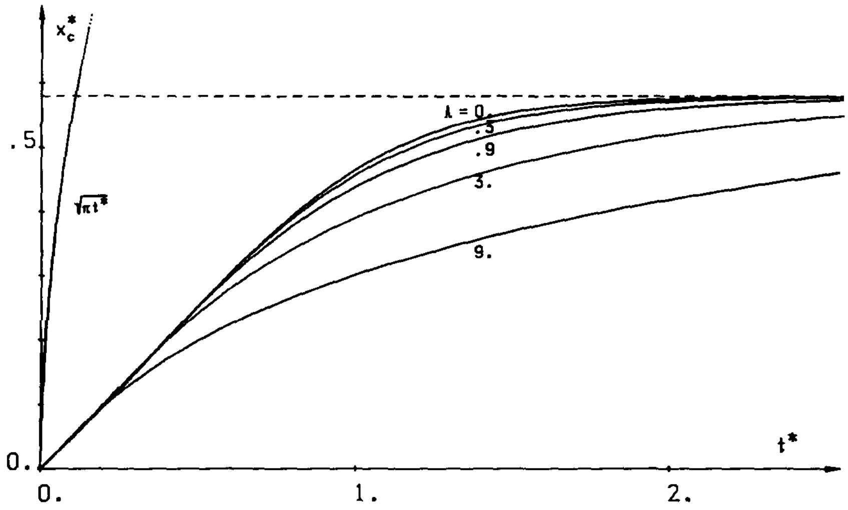

Fig. 1: Reduced distance of crystallization front from cold wall against Fourier number (= reduced time) for various values of Λ, including the realistic value 0,9. Neumann's solution is indicated at the left side. For finite gap width D it should level off at the dashed line.

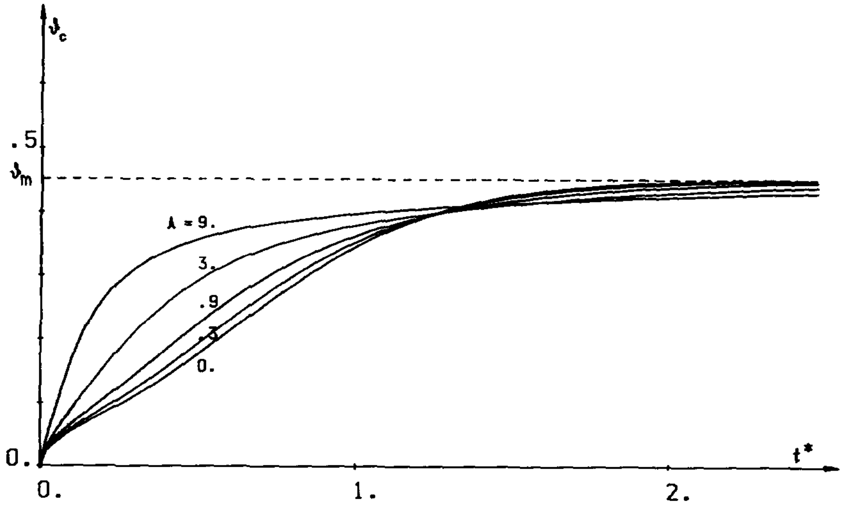

Fig. 2: Reduced temperature at crystallization front against Fourier number for various values of Λ. According to the classical approach this reduced temperature should be time independent and at the level of the dashed line.

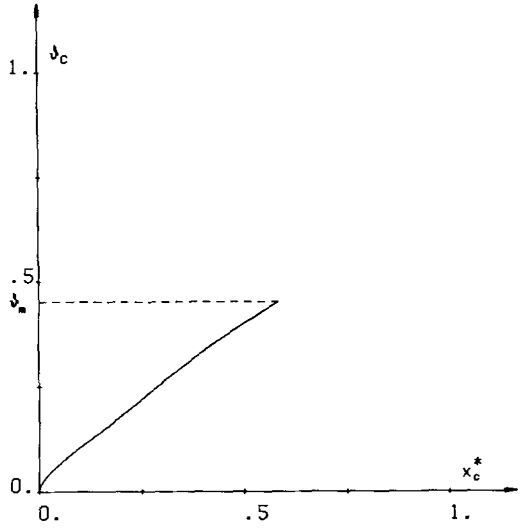

Fig. 3: Reduced temperature at crystallization front against reduced distance of this front from the cold wall for Λ = 0,9 after elimination of reduced time from Figs. 1 and 2.

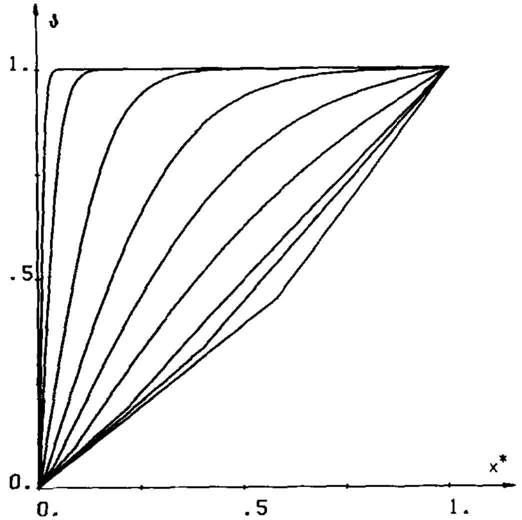

Fig. 4: Complete temperature profiles for Λ = 0,9. (Reduced temperature vs. reduced x-coordinate.) The curves from left to right belong to Fourier numbers 0,0001; 0,001; 0,01; 0,03; 0,1; 0,2; 0,4; 1,0 and ∞. By connecting the kinks of the curves one obtains Fig.3.

contributions to the discussion and for furnishing an approximate analytical solution of highly encouraging value. They are also very grateful to Mr. G. Krobath for making his experimental experience available. To the Austrian "Fonds zur Förderung der Wissenschaftlichen Forschung" we are grateful for financial support (P 4819).

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