



0017-9310(94)00205-3

Energy equation and the crystallization kinetics of semi-crystalline polymers: regimes of coupling

A. BÉNARD and S. G. ADVANI†

Department of Mechanical Engineering, University of Delaware, Newark, DE 19716, U.S.A.

(Received 17 February 1994 and in final form 1 July 1994)

Abstract—The processing conditions play an important role in the development of the crystallinity of thermoplastic polymers and the energy equation describing the heat transfer problem can be strongly coupled to the material kinetics. In this paper, the importance and nature of the coupling is evaluated by comparing the temperature and crystallinity distributions obtained from a fully coupled zone model (considered as the most general approach) with two cases: Neumann's solution (sharp interface-moving boundary) and the one-domain diffusion equation with no heat generation (uncoupled solution). Two non-dimensional parameters, Stefan's (St) and Deborah's (De) numbers, that play a key role in determining the extent of the coupling, are isolated. The influence of the coupling and its nature have been demonstrated numerically in selected cases. Results of the parametric studies show that De and St decide the nature of the coupling. The error made by decoupling the problem can be shown graphically and regimes are identified where the coupling is important or negligible. Criteria allowing the identification of the regimes are presented. Finally, an example is presented to demonstrate the importance of the coupling for the cooling of Nylon 6-6 and PET, which exhibit fast and slow crystallization kinetics.

INTRODUCTION

Unlike other materials, the solidification of semi-crystalline polymers is convoluted due to the strong dependence of the nucleation and growth of polymeric crystals on the cooling conditions. The crystal kinetics depend not only on the temperature but may be a strong function of other material and process parameters such as the rate of cooling, type of polymer and the state and orientation of the polymer chains.

The macroscopic approaches used for modelling the solidification of polymers can be broadly divided into three categories: uncoupled approach, sharp moving boundary approach and the zone models. The first approach models the solidification in polymers by ignoring the heat generated due to the latent heat release as it can be a small fraction of the total heat transfer involved during the cooling process. Hence, the heat flow is modeled by a heat diffusion equation written for the solid and liquid domain with no heat generation term. The energy equation in such cases will be decoupled from the kinetics of the polymer. The evolution of the microstructure is found from the temperature field. This approach has the advantage of being easy to implement, it requires a minimum amount of computations and it does have a closed form solution for selected boundary conditions [1]. A variation of this approach has been to modify the specific heat when one goes from a liquid domain to a solid domain to account for the heat of fusion [2].

The second approach has adopted classical moving boundary solutions to model the solidification of polymers. The classical approach was first used by Stefan [3] and later modified by Neumann [4] for semi-infinite domains and a closed form solution was found which is known as Neumann's or/and Stefan's solution. In this approach the domain is sharply divided in a solid and liquid zone and the crystallization kinetics are perceived as an "on" or "off" phenomenon. Therefore, one clearly delineates the solid domain from the liquid domain via a sharp boundary. The energy equations are solved in both domains and coupled via an energy balance at the interface. However, this approach is somewhat limited for semi-crystalline polymers as it does not account for the changing polymer kinetics during the cooling process and the crystallization front does not always propagate as a well-defined boundary [5, 6]. A variation of this approach, to account for changing crystallinity during cooling, was the introduction of a variable interface temperature to couple the material kinetics with the heat diffusion process [7–9]. It was found, however, that the sharp interface assumption does not always hold.

The third approach of zone models was introduced for polymers by Berger and Schneider [10], Astarita and Kenny [11, 12] and Eder *et al.* [6] among others. With these models, it is possible to simulate the crystallization process as a propagating zone that can be very large (the complete domain) or very narrow (a sharp interface), depending on the processing conditions and material parameters. The crystallization

† Author to whom correspondence should be addressed.

NOMENCLATURE

C_p	specific heat capacity at constant pressure [kJ kg ⁻¹ K ⁻¹]	T^*	dimensionless temperature, $(T - T_g)/(T_i - T_g)$
D	crystallization kinetics parameter [K]	T_g	glass transition temperature [K]
De	thermal Deborah number, $\alpha t_c/L^2$	T_i	initial temperature [K]
f_s	volume solid fraction	T_m	melt temperature [K]
H	enthalpy [kJ kg ⁻¹]	x^*	dimensionless position, x/L .
H_f	heat of fusion [kJ kg ⁻¹]		
k	thermal conductivity [W m ⁻¹ K ⁻¹]	Greek symbols	
L	half-thickness [cm]	α	coefficient of thermal diffusivity [m ² s ⁻¹]
m	crystallization parameter	λ	Neumann's solution parameter [cm]
n	crystallization parameter	ρ	specific volume [kg cm ⁻³]
p	crystallization parameter	χ	relative crystallinity, $\chi_{\text{actual}}/\chi_{\infty}$
q'	heat generation term [kJ m ⁻³ s ⁻¹]	χ_{∞}	equilibrium crystallinity.
St	Stefan's number, $H_f/C_p/(T_i - T_g)$	Subscripts	
t	time [s]	i	initial value
t^*	dimensionless time, t/t_c	w	cold wall.
t_c	crystallization characteristic time [s]		
t_{\min}	minimum crystallization half-time [s]		
$t_{1/2}$	crystallization half-time [s]		

kinetics of the polymer are coupled with the energy equation through a heat generation term in the zone model. How one models this heat generation term depends on how the crystallization kinetics are described. The zone models warrant a numerical solution and become fairly cumbersome and computationally expensive when the phase change zone becomes very narrow. Neumann's solution under such conditions is fairly accurate and has a closed form solution. Thus, it is important to identify conditions under which the zone becomes very thin so one can take advantage of a closed form solution.

The experimental findings have supported the first approach (uncoupled solution) and the second approach (Neumann's solution) under certain cooling conditions. However, for many semi-crystalline materials, the results have been less than satisfactory with the first or the second approach [6]. This scenario points to the fact that there may be regimes of cooling and temperatures for which one may have to couple the kinetics with the energy equation and resort to zone models to predict the temperature and the crystallinity distributions of the material as a function of the temperature history.

The objective of this work is to identify the regimes and conditions under which one should couple the kinetics and the energy equation for such materials. Our intent is to examine the importance of coupling the crystallization kinetics of the polymer with the energy equation and study the nature of this coupling. These considerations are important since uncoupled solutions or Neumann's solutions are often used to compute residual stresses (which depend on the temperature history of the material) and analyze experimental data. In cases where this coupling is significant, considerable errors can be introduced in

calculating of the temperature field by use of uncoupled solution or assumption of a sharp boundary between the solid and liquid domains.

In this paper, the importance and nature of the coupling is evaluated by comparing the temperature and crystallinity distributions obtained from a fully coupled zone model (considered as the most general approach) with two cases: Neumann's solution (sharp interface-moving boundary) and the one-domain diffusion equation with no heat generation (uncoupled solution). Two non-dimensional parameters, Stefan's number and Deborah's number, that play a key role in determining the extent of coupling, are isolated. Parametric studies are conducted to identify the regimes of coupling as a function of these two numbers. The cooling of PET and Nylon 6-6, both semi-crystalline materials with significantly different kinetics, is modeled with the zone model to show how the kinetics can change the temperature history and crystallinity under identical external conditions. This should caution the processing engineer to take into account the microstructure when designing the cooling characteristics.

PHASE CHANGE MODELS

Most polymers are cooled in the form of sheets or parts with their length and width much larger than their thickness. Hence, the cooling is usually isothermal in the plane and may be considered as a one-dimensional phenomenon in the thickness direction. As our goal is to identify regimes of coupling and understand the coupling, we restrict our attention to one-dimensional problems. The results may be extended to multi-dimensional cooling with caution.

The approach here is to solve for the temperature

using all three approaches : a zone model in which the energy equation is written for the whole domain with a heat generation term, a decoupled model in which the energy equation and the kinetics are decoupled and Stefan's approach (or Neumann's solution) in which the domain is sharply divided in a solid and liquid zone and where the crystallization kinetics are perceived as being an "on" or "off" phenomenon.

We present the formulation for each of these models below and isolate the Stefan's and Deborah's numbers.

Zone model

The zone models are based on the postulate that the total heat content (sum of specific heat and latent heat required for a phase change) can be represented by an enthalpy function such as

$$H(T) = \int_{T_0}^T \rho(\theta)C_p(\theta) d\theta + \rho H_f(1-f_s(T)) \quad (1)$$

where C_p is the heat capacity, ρ the density, T_0 a fixed temperature below the melting point and H_f the heat of fusion of the material. The discontinuity normally encountered at a macroscopically well defined interface is smoothed by the function describing the evolution of the solid fraction $f_s(T)$, in a manner similar to the enthalpy smoothing methods summarized by Crank [13]. This allows one to account for the presence of a "mushy" zone between the fully solid zone and the fully liquid zone. This approach is useful when there is no well-defined boundary at a macroscopic level between the solid and liquid zones, which has been observed to be the case for many semi-crystalline polymers [6]. The time derivative of equation (1) gives

$$\frac{\partial H(T)}{\partial t} = \rho C_p \frac{\partial T}{\partial t} - \rho H_f \frac{\partial f_s}{\partial t} \quad (2)$$

where ρ and C_p are assumed to be constant for simplicity.

Consider the crystallization of a slab of polymer melt of half-thickness L with both of its external surfaces exposed to a temperature below the melting temperature at time zero. The degree of crystallinity χ can take values ranging between 0 (no crystallinity) and 1 (equilibrium crystallinity, i.e. the maximum crystallinity that can be reached for a given polymer). For this one-dimensional, transient heat transfer problem, the balance of energy can then be written as

$$\rho C_p \frac{\partial T}{\partial t} = k \frac{\partial^2 T}{\partial x^2} + q' \quad (3)$$

where q' models the heat generation term and depends on the crystallization rate of the polymer :

$$q' = \rho H_f \frac{\partial \chi}{\partial t} \quad (4)$$

with initial conditions

$$t = 0 \quad T = T_i = T_m \quad \text{for} \quad 0 \leq x \leq L.$$

The constitutive equation for the crystallization rate ($\partial \chi / \partial t$) in equation (4) is derived from the kinetics of nucleation and growth of crystals in semi-crystalline polymeric materials and it may be a strong function of the temperature and cooling rate. The heat generated by the latent heat release can also affect locally the temperature profile, thus underlying the coupling of equation (3) with equation (4). For the case of a constant wall temperature, the boundary conditions for equation (3) are

$$x = 0 \quad T = T_w \quad \text{and} \quad x = L \quad \frac{\partial T}{\partial x} = 0.$$

This problem contains two independent variables, time (t) and position (x); two dependent variables, temperature (T) and crystallinity (χ); and six material constants, density (ρ), thermal conductivity (k), heat capacity (C_p), heat of fusion (H_f), glass transition temperature (T_g) and a crystallization characteristic time (t_c). T_g is the temperature that signifies a change for the amorphous regions of polymer from a rubber-like state to a glassy state where the molecules have limited mobility. Furthermore, t_c is small for fast crystallizing polymers and high for slow crystallizing polymers. Three process parameters also appear : the slab half-thickness (L), the initial temperature (T_i) and the wall temperature (T_w). All material parameters are assumed to be independent of temperature to focus on the objective of the analysis.

The equations can be rendered dimensionless by dividing each variable with a characteristic value. Thus, we can define $x^* = x/L$, $t^* = t/t_c$ and a dimensionless temperature as $T^* = (T - T_g)/(T_i - T_g)$. Here we should point out that an alternative option to render time dimensionless is $\alpha t/L^2$. However, as our goal is to explore the influence of material kinetics, we use t_c as the characteristic time. Thus, using these characteristic values, the governing heat balance equation (3) can be cast in the dimensionless form

$$\frac{\partial T^*}{\partial t^*} = De \frac{\partial^2 T^*}{\partial x^{*2}} + St \frac{\partial \chi}{\partial t^*} \quad (5)$$

with the boundary conditions of constant wall temperature, expressed in non-dimensional variables, as :

$$x^* = 0 \quad T^* = T_w^* \quad \text{and} \quad x^* = 1 \quad \frac{\partial T^*}{\partial x^*} = 0.$$

In equation (5), De is the thermal Deborah number ($De = \alpha t_c/L^2$) [11], similar to the Deborah number that describes the elasticity of a viscoelastic fluid. The Deborah number is the ratio of a characteristic time scale for a morphological change to occur (t_c) over the heat diffusion time scale (L^2/α). A small De number implies that the kinetics of a polymer are fast (low t_c) compared to the heat diffusion process. St is the Stefan number ($St = H_f/(C_p(T_i - T_w))$). The Stefan number is the ratio of the latent heat to the specific heat and the imposed temperature difference. A large Stefan number signifies that the heat released during the

phase transition is absorbed very slowly by the material as a result of a variation of the sensible heat content.

To describe the temperature in such materials, one needs to describe the mechanisms of nucleation and growth of polymeric crystals by a constitutive equation that will describe the overall crystallization rate. Different constitutive equations have been proposed for the non-isothermal crystallization rate equation [14]. We consider a form similar to a model presented by Astarita and Kenny [11]:

$$\frac{\partial \chi}{\partial t^*} = (1 - \chi)^m T^{*n} (1 - T^*)^p, \quad 0 < T^* < 1. \quad (6)$$

This equation is geared toward satisfying the requirement that the rate tends to zero as χ tends to one. Also, crystallization can occur only if the temperature is between the melt temperature and the glass-transition temperature. Formation of the crystals is possible only if the temperature is below the melting point and growth of crystals ceases with the temperature falls below the glass transition temperature. Here, m , n and p will change the dependence of the crystallization rate on the degree of crystallinity and its sensitivity to the temperature and will be characteristic of the material to be modeled.

Uncoupled formulation

For a material with low heat of fusion and a very large crystallization zone, the heat generation term is often assumed to be small and neglected. The dimensionless heat diffusion equation then takes the form

$$\frac{\partial T^*}{\partial t^*} = De \frac{\partial^2 T^*}{\partial x^{*2}}. \quad (7)$$

The exact solution, with the conditions of a constant wall temperature T_w^* at $x^* = 0$ and an initial temperature $T_1^* = 1$, is given by a Fourier series type of solution:

$$T^* = T_w^* + \frac{4(1 - T_w^*)}{\pi} \times \sum_{n=1}^{\infty} \left\{ \exp\left(\frac{-n^2 \pi^2 t^* De}{4}\right) \sin\left(\frac{n \pi x^*}{2}\right) \right\} \quad (8)$$

where $n = 1, 3, 5, \dots$. The crystallinity profile is obtained, after the solution of equation (8), by integrating equation (6), i.e.

$$\int_{\chi_0}^{\chi} \frac{d\chi}{(1 - \chi)^m} = \int_{t_0}^{t_i} T^{*n} (1 - T^*)^p dt. \quad (9)$$

To numerically integrate equation (9), the simple Euler rule may be used in which the temperature is assumed to be constant over a small time interval $(t_{i+1} - t_i)$. This results in

$$\chi = 1 - (1 - \chi_i) e^{-T^{*n}(1 - T^*)^{p}(t_{i+1} - t_i)} \quad (10)$$

where χ_i is the crystallinity at t_i . The exponents m, n and p in equation (6) are set to 1 for this case.

Neumann's solution

At the other extreme, the solidification of a polymer can be treated as a narrow zone and hence a front tracking method can be utilized. The well-known Neumann's solution provides an analytical solution for the solidification of a semi-infinite domain. The problem at hand may be solved approximately by using this solution. In a domain of finite length L , this solution is valid only at small time scales due to the hypothesis of a semi-infinite domain. However, to solve the problem at large time scales, it is recommended to use a numerical method such as the methods presented by Murray and Landis [15]. The solutions given by Neumann's solution (presented below) were all checked against the technique of Murray and Landis.

Consider a semi-infinite domain divided in two regions: the solid region and the liquid region. At time $t^* = 0$, the boundary surface at $x^* = 0$ is quenched to a temperature T_w^* below the melt temperature. The solidification then starts at $x^* = 0$ and the solid-liquid interface moves in the positive x^* -direction. The temperature distribution in the solid and liquid zones, with the position of the interface, are obtained from the Neumann's solution [1, 16]. The temperature distribution of the solid phase is given as

$$T^*(x^*, t^*) = T_w^* + (1 - T_w^*) \frac{\text{erf}(x^*/2(t^* De)^{1/2})}{\text{erf}(\lambda)} \quad (11)$$

when the liquid zone is initially at the melt temperature. All parameters of the problem have been rendered dimensionless as in the coupled formulation.

An energy balance made at the interface is used to determine the relation needed to evaluate the parameter λ . The following transcendental equation is obtained:

$$\frac{(1 - T_w^*)e^{-\lambda^2}}{\text{erf}(\lambda)} = \lambda \pi^{1/2} St. \quad (12)$$

Once λ is known, the temperature distribution can be found and the position of the interface $s^*(t)$ is determined from

$$s^*(t) = 2\lambda(t^* De)^{1/2}. \quad (13)$$

The material is assumed to achieve its maximum crystallinity immediately after the passage of the front and the interface temperature always stays at the equilibrium melt temperature.

The velocity of the front is obtained by taking the derivative with respect to time of equation (13) and, at very small process times, it can be observed that this velocity goes to infinity. Since no process occurs at an infinite speed in nature, this approach is not valid at very small process times. This phenomenon is in accordance with the assumption that heat propagates at an infinite speed in a solid. Nonetheless, this

solution will be useful later in providing a bound to the possible regimes of coupling.

NON-ISOTHERMAL COUPLING

Order-of-magnitude analysis

The morphological changes that take place in a polymer can occur either as a sharp interface or as a very diffuse zone. It has been shown that the ratio of the Stefan number to the Deborah number, the Janeschitz-Kriegl (*JK*) number as coined by Astarita and Kenny [11], will determine the type of morphological change in the material. A scaling analysis of the governing equation will indeed confirm that the ratio of the *St* and *De* is important in describing the behavior of the system. It also reveals that, in addition to the ratio, *St* and *De* independently play a role in the nature and extent of the coupling. Scaling the equation will help to identify the conditions under which the heat diffusion and the crystallization kinetics mechanisms should be coupled and the nature of this coupling.

We can scale the temperature with the temperature difference $\Delta T = (T_i - T_g)$, the time with the crystallization characteristic time t_c , and the *x*-coordinate with the length of the domain *L*. The crystallinity is already scaled with the equilibrium crystallinity (of order one). The order-of-magnitude counterpart of equation (3) becomes:

$$\underbrace{\frac{\Delta T}{t_c}}_{\text{transient term}} \sim \underbrace{\frac{\alpha \Delta T}{L^2}}_{\text{steady-state term}}, \quad \underbrace{\frac{H_f}{C_p t_c}}_{\text{kinetics term}} \quad (14)$$

This equation can be rearranged in terms of *St* and *De*:

$$\underbrace{\frac{1}{St}}_{\text{transient term}} \sim \underbrace{\frac{De}{St}}_{\text{steady-state term}}, \quad \underbrace{1}_{\text{kinetics term}} \quad (15)$$

The last equation can help, in a qualitative manner, to identify the various regimes of the system when the time scale is of the order of t_c . For example, if $St \rightarrow 0$ the transient aspect of the problem will be balanced by the steady-state term and the kinetics do not influence the system, as expected. The system is then reduced to the simple transient heat diffusion equation where the uncoupled formulation may be used. If $De \rightarrow 0$, the transient term is balanced by the kinetics term, and both the cooling rate and the crystallization kinetics will be dominant and will influence each other. Also, if $St \rightarrow 0$ and $De \rightarrow 0$, it implies that the cooling rate of the domain must be very small to satisfy the equality. Although the steady-state and kinetics terms are then of the same order, the transition is happening at such a slow pace that very little differences are to be expected between coupled and uncoupled approaches. The transient term will be more significant for time scales less than t_c and will become less important as time becomes larger than t_c .

This analysis of the equation offers qualitative understanding of the nature of the interactions and also shows that it is not only the ratio of *St/De* but that the role of both numbers independently is also important. However, by conducting numerical simulations of the differential equation, one can bring forward the possible regimes of coupling between the energy equation and the crystallization kinetics in a quantitative manner.

Numerical experiments

The importance and nature of the coupling can be determined by comparing the temperature and crystallinity distributions obtained by solving equation (5) with equation (8) (uncoupled formulation) and equation (11) (Neumann's formulation).

The exact solution of (5) is in the form of a Volterra integral equation of the second kind. To solve the integral equation emerging from (5), one has to use numerical integration. However, we resorted to finite differences since it is a technique that is easier to program and the implicit Crank-Nicholson scheme was used. A time-step of 10^{-3} was used and the domain was divided in 100 elements. All the runs converged with these values and no differences were found by reducing them. The crystallization kinetics, given by equation (6), can be computed as in equation (10) or by using a Runge-Kutta algorithm. Since the temperature and the crystallinity are two dependent variables, they both need to be solved simultaneously and an iterative scheme was used for this purpose.

Numerous combinations of the dimensionless parameters, *St* and *De*, are possible and we studied a large number of cases for values of *De* and *St* numbers ranging from 10^{-4} to 1. However, to bring forward the possible regimes of coupling, it suffices to look at the following cases:

- case 1: $De = 10^{-4}$ $St = 10^{-4}$ ($De \rightarrow 0, St \rightarrow 0$);
- case 2: $De = 1$ $St = 10^{-4}$ ($De \sim 1, St \rightarrow 0$);
- case 3: $De = 10^{-4}$ $St = 1$ ($De \rightarrow 0, St \sim 1$);
- case 4: $De = 1$ $St = 1$ ($De \sim 1, St \sim 1$).

The crystallization kinetics are given by equation (6), with the exponents *m*, *n* and *q* set to 1. This rate equation peaks at a crystallinity of zero and a dimensionless temperature of 0.5. A wall dimensionless temperature of 0.1 was chosen. Numerical results corresponding to the above cases are presented in the next section.

RESULTS AND DISCUSSION

Temperature and crystallinity profiles

The temperature and crystallinity profiles obtained for the above cases are presented in Figs. 1-4. An illustration of the problem being considered is presented over each of these figures to facilitate the interpretation of the results.

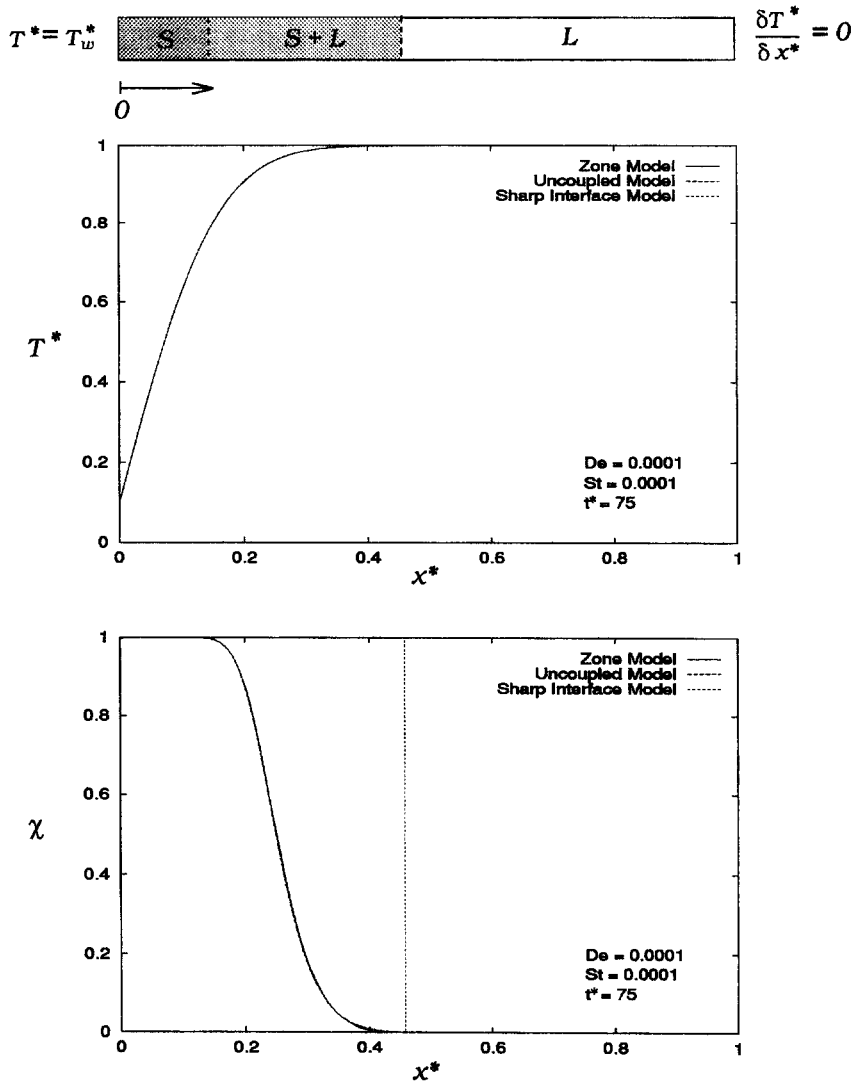


Fig. 1. Temperature (T^*) and crystallinity (χ) profiles in the domain at a dimensionless time $t^* = 75$ obtained using Stefan's approach, the uncoupled approach and the coupled zone formulation.

It can be seen that, for case 1, the three temperature profiles are identical. This is to be expected since St is so small that any heat generation effect on the temperature is negligible. Furthermore, the small De implies that the sharp interface approach is also valid for the temperature profile since the solidification process occurs extremely slowly with almost no heat generation. Hence any approach may be used in this regime since the temperature solutions matched at all times during the transient calculations. The crystallinity profile computed from the coupled formulation can not be distinguished from the profile obtained from the uncoupled heat diffusion equation, showing that the coupling is very weak. However, since Stefan's approach (Neumann's solution) requires a sharp front, a weakness of the sharp interface assumption is shown here as the interface is located where the phase transformation has just started, i.e. at a location where no crystallites have

formed yet. However, as De and St both get smaller, this error is reduced since the crystallizing zone also becomes smaller. The position of the interface and the temperature profile were also verified with the finite-difference scheme of Murray and Landis [15] and no discrepancies were found. The temperature and crystallinity profiles are shown for a rather large dimensionless time of 75 since the cooling process is slow.

For the second case, St is very small (10^{-4}) and the uncoupled heat diffusion equation gives an excellent approximation of the temperature profile. The temperature profile given by Neumann's solution is much higher than the other formulations, due to the assumption of a semi-infinite domain. Here, the results have been shown at the early stage of cooling. However, it was found that the Neumann's solution continued to diverge from the correct solution with time. The second case shows that, since St is very small, the heat generated by the phase transformation can be

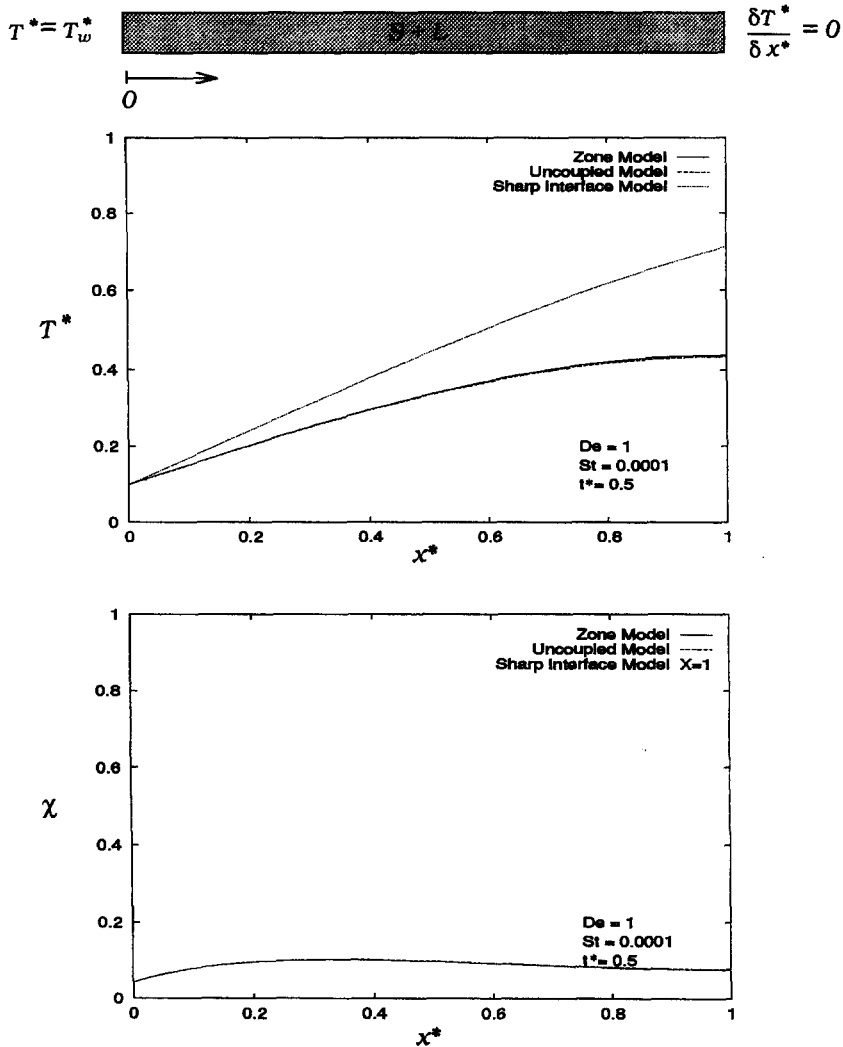


Fig. 2. Temperature (T^*) and crystallinity (χ) profiles in the domain at a dimensionless time $t^* = 0.5$ obtained from Stefan's approach, the uncoupled approach and the coupled zone formulation.

neglected and the crystallinity profile computed from the uncoupled heat diffusion equation is an excellent approximation. The crystallinity profiles are shown at a small value of dimensionless time and follow each other closely throughout the process.

The third case presents a situation treated by Astarita and Kenny [11] where the ratio of $St/De \rightarrow \infty$. St is 1 and hence the kinetics term is not negligible and the crystallization process occurs over a small portion of the domain. This situation arises if the Jk number (St/De) is large, as discussed in [11]. The temperature profile, in this case, is heat diffusion controlled and since the crystallization kinetics are restricted to a narrow zone of the domain, Stefan's approach is valid since the zone model approaches Neumann's solution. Figure 3 shows the crystallinity profiles. The crystallinity profile computed from the uncoupled heat diffusion equation overestimates the position and size of the crystallization zone. There is no heat generation in this formulation to slow down the cooling process

and the movement of the interface, hence it cannot be used in this regime. The crystallinity and temperature profiles are shown again for a dimensionless time of 75 since the cooling process is very slow.

The final case of De and $St \sim 1$ shows that Stefan's approach and the uncoupled solution diverge considerably from the coupled approach. The temperature profile for this case is presented in Fig. 4 for a dimensionless time of 0.5. Stefan's approach is not valid in this regime since the transformation occurs over a large zone and the simple heat diffusion equation (uncoupled approach) does not hold since it does not take into account the heat generated by the crystallization process over the time scale considered. Hence, it is necessary to couple the heat flow and the crystallization kinetics for such cases. The crystallinity profiles, presented in Fig. 4, show that the profiles computed from the three approaches are very different. The whole domain crystallizes almost uniformly, showing that a sharp interface approach does not

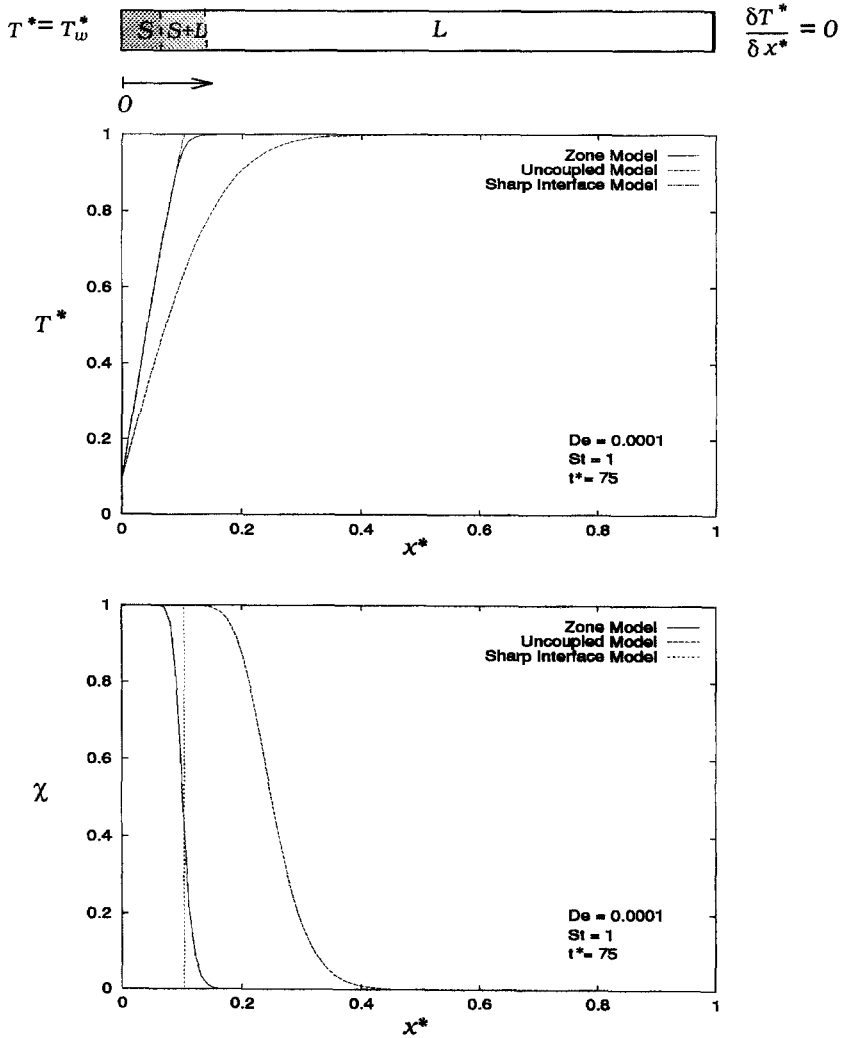


Fig. 3. Temperature (T^*) and crystallinity (χ) profiles in the domain at a dimensionless time $t^* = 75$ obtained from Stefan's approach, the uncoupled approach and the coupled zone formulation.

hold. Using the uncoupled heat diffusion equation to compute the crystallinity profile underestimates the level of crystallinity since the kinetics are dependent on the temperature which in turn are also influenced by the phase transformation process. Figure 4 shows the process for a dimensionless time of 5, since, at very early stages, the two crystallinity profiles are almost identical but diverge as the heat generation term becomes more important. For such cases, the two-way coupling accelerates the crystallization kinetics, a phenomenon not accounted for if the simple uncoupled formulation is used.

Regimes of coupling

The four cases shown from the parametric study clearly identify regimes where the energy equation and the crystallization kinetics may be decoupled and where the approach of a sharp interface is valid. These regimes can be determined with the De and St and one can avoid the time consuming approach of solving

two coupled equations for these regimes. Furthermore, as the ratio St/De becomes large, the discontinuity introduced by a sharp interface causes numerical problems in this one-domain formulation and it is then preferable to use a two-domain numerical scheme or to use the Neumann's solution if applicable. It is also helpful in the analysis of experimental data to identify cases where the crystallization process considered exhibits a strong coupling with the heat diffusion process.

The various domains or regimes of coupling are represented graphically in Fig. 5 for the temperature and in Fig. 6 for the crystallinity. To establish these regimes, many parametric studies were conducted for De and St ranging from 0 to 1.

A first regime can be observed for the case of St being less than 0.1. For these low values of St , the heat diffusion equation can be decoupled from the crystallization kinetics without introducing large errors. It is essential to couple both formulations at

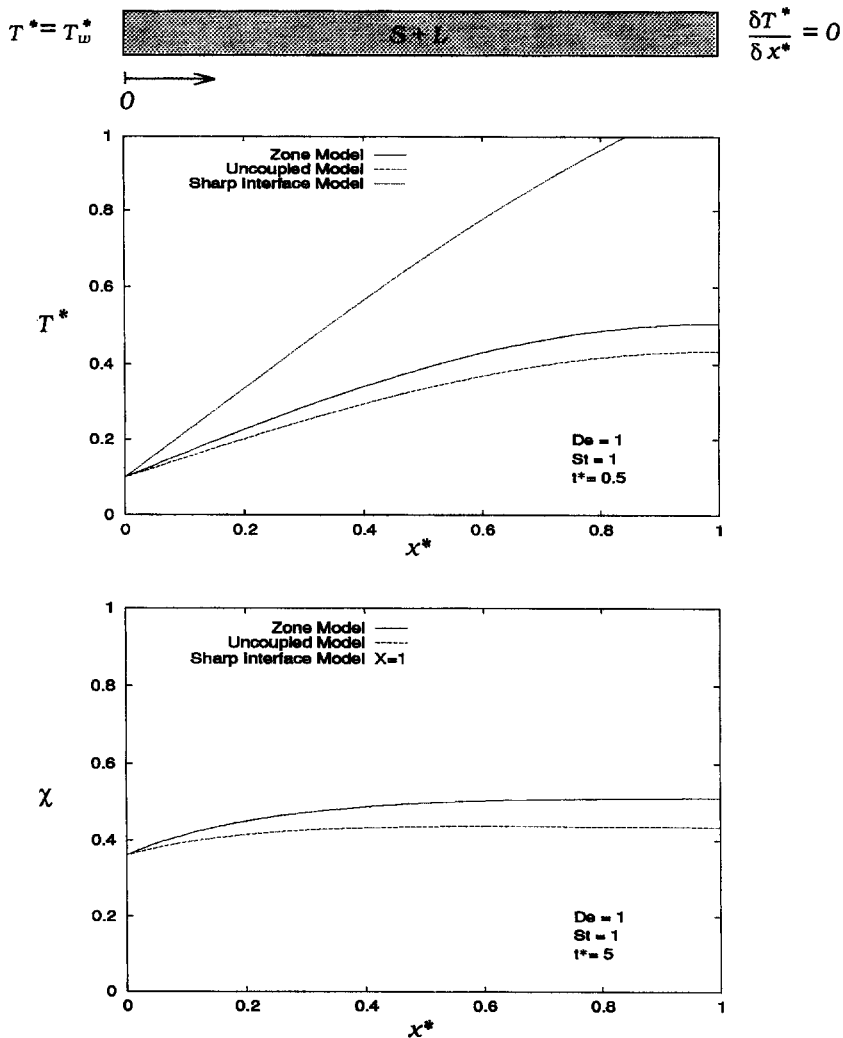


Fig. 4. Temperature (T^*) profile in the domain at a dimensionless time $t^* = 0.5$ and crystallinity (χ) profile at a dimensionless time $t^* = 5$ obtained from Stefan's approach, the uncoupled approach and the coupled zone formulation.

larger values of St , otherwise the temperature and crystallinity profiles obtained will be erroneous.

At very low values of De , which is not an uncommon situation, the coupled formulation shows a very good agreement with the sharp interface approach for the crystallinity and the temperature profiles, suggesting the presence of another regime. To obtain an excellent match in temperature and crystallinity, the De must have values in the range of 10^{-3} . However, the temperature does match well even at values of $De = 0.1$ for parts of the domain where $\chi > 0.5$.

At low values of St and De , a fourth regime can be identified where coupled and decoupled approaches give identical solutions for the temperature distributions.

To demarcate the regimes, approximate lines have been drawn in Figs. 5 and 6 where it might be possible to use an alternative formulation to the coupled equations without introducing considerable errors in the

computed temperature and crystallinity profiles. In these regimes, the coupling will be weak and the energy equation can be solved independently of the kinetics.

EXAMPLES

To assess the validity of the regimes mentioned above for semi-crystalline polymers, the cooling of PET and Nylon 6-6 was studied in a plaque of 1 cm thickness ($L = 0.5$ cm). PET and Nylon 6-6 have respectively slow and fast crystallization rates. The cooling of the melt is obtained by maintaining a dimensionless wall temperature of $T^* = 0.5$.

The material properties used for the computations are given in Table 1 and were obtained from [17, 18]. The Stefan number was computed with $\chi_\infty H_f$ since the heat of fusion is assumed to be given for a perfect polymer crystal.

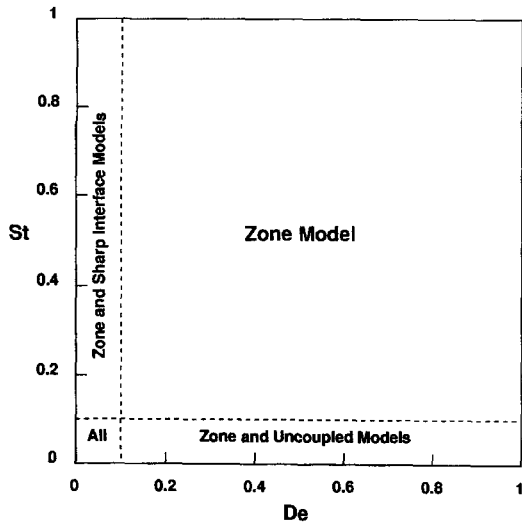


Fig. 5. Regimes of validity for the temperature profiles of various approaches as a function of the Deborah and the Stefan numbers.

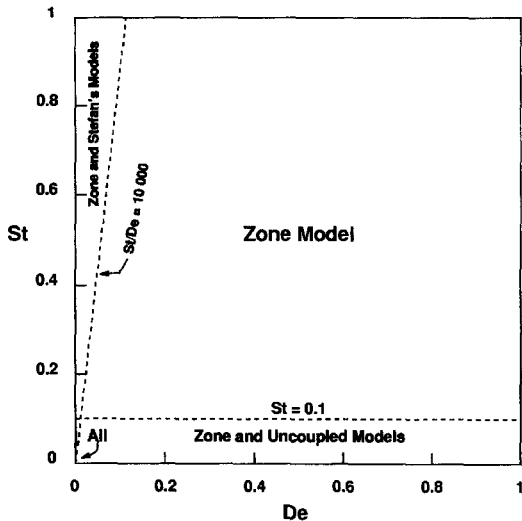


Fig. 6. Regimes of validity for the crystallinity profiles of various approaches as a function of the Deborah and the Stefan numbers.

The crystallization kinetics equation used for the computations is taken from Ziabicki [17]. This equation has the form

$$\frac{d\chi}{dt} = nK(T)(1-\chi) \left[\ln \left(\frac{1}{1-\chi} \right) \right]^{(n-1)/n} \quad (16)$$

where

$$K(T) = \frac{1}{t_{\min}} \exp \left[-4 \ln 2 \frac{(T - T_{\max})^2}{D^2} \right]. \quad (17)$$

In equation (16), $\chi = \chi_{\text{actual}}/\chi_{\infty}$, t_{\min} is the minimum crystallization half-time and is used as t_c to calculate De , D and n are both kinetics parameters.

The crystallization rate exhibited by equation (16)

Table 1. Material properties and parameters used in the examples

Properties	PET	Nylon 6-6
H_f [J g ⁻¹]	125	205
T_m [°C]	267	264
T_g [°C]	67	45
ρ [kg cm ⁻³]	1.385	1.14
C_p [J g ⁻¹ K ⁻¹]	1.4	0.46
k [W cm ⁻¹ K ⁻¹]	0.0014	0.00245
α [cm ² s ⁻¹]	0.00063	0.00463
$t_{1/2}$ [s]	42	0.42
χ_{∞}	0.40	0.45
n	2	2
T_{\max} [°C]	190	150
D	64	80
De	0.11	0.0078
St	0.18	0.92
$JK = [St/De]$	1.6	118

is similar to equation (6) as they both have a bell-shaped form when crystallinity is plotted on the y axis and temperature is on the x axis. This form has been found to describe adequately the crystallization kinetics of numerous semi-crystalline polymers [17]. The parameters required to compute the crystallization rates using equation (16) are given in Table 1. These parameters are also obtained from [17].

To be compatible with the dimensionless form of the energy equation, the crystallization kinetics equation is written as

$$\frac{d\chi}{dt^*} = nt_{\min} K(T)(1-\chi) \left[\ln \left(\frac{1}{1-\chi} \right) \right]^{(n-1)/n}. \quad (18)$$

The temperature and crystallinity profiles of PET and Nylon 6-6 have been computed with the zone model, uncoupled formulation and Neumann's solution (Stefan's approach). According to Figs. 5 and 6, for the St and De of these examples, the sharp interface and the uncoupled models should be marginally acceptable in computing the temperature profile for $\chi > 0.5$. This can be seen from Figs. 7 and 8. The temperature profile can be well approximated with Neumann's solution (sharp interface) for parts of the domain where $\chi > 0.5$, as shown in Figs. 7 and 8, while the crystallinity profile is not rendered very well. The uncoupled approach also gives marginally acceptable results: however, the gap in the temperature profiles between the coupled and uncoupled models increases at larger time scales. Thus, a coupled approach should be used for Nylon 6-6 and PET. The uncoupled approach can only be used for the initial stages of the cooling process. Stefan's approach would give good results with these materials only if the plaque were significantly thicker, which would reduce the magnitude of the thermal De .

Finally, cooling profiles can easily be computed from the previous calculations and are useful to understand the effect of the crystallization process on the local temperature. Such profiles are presented in Fig.

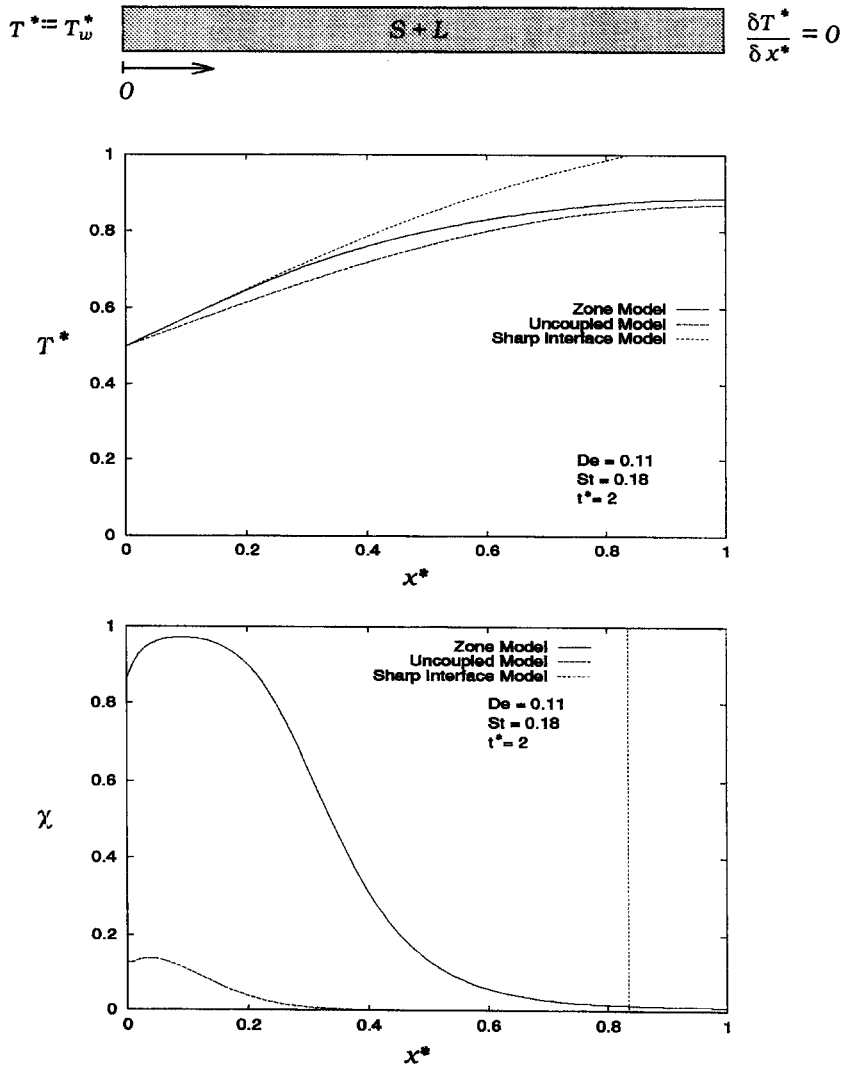


Fig. 7. Temperature (T^*) and crystallinity (χ) profiles in the domain at a dimensionless time $t^* = 2$, computed for PET with the zone model, the sharp interface model and the decoupled model.

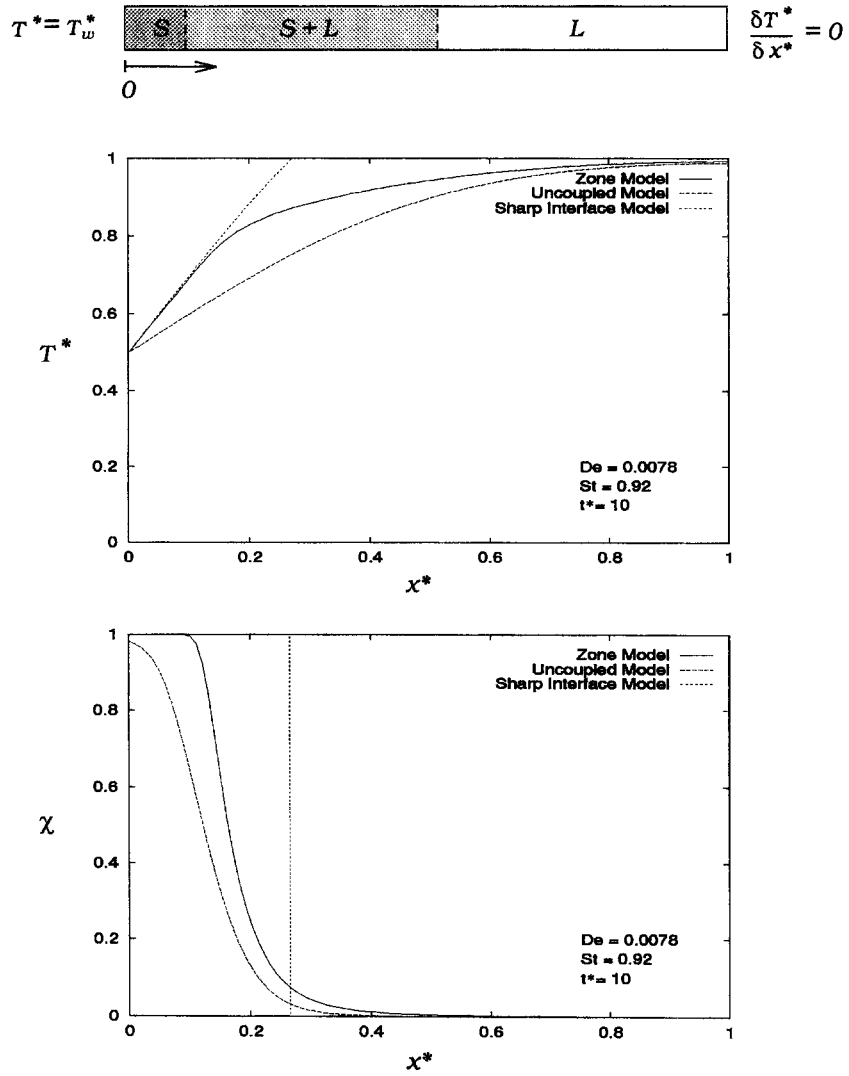


Fig. 8. Temperature (T^*) and crystallinity (χ) profiles in the domain at a dimensionless time $t^* = 10$, computed for Nylon 6-6 using the zone model, the sharp interface model and the decoupled model.

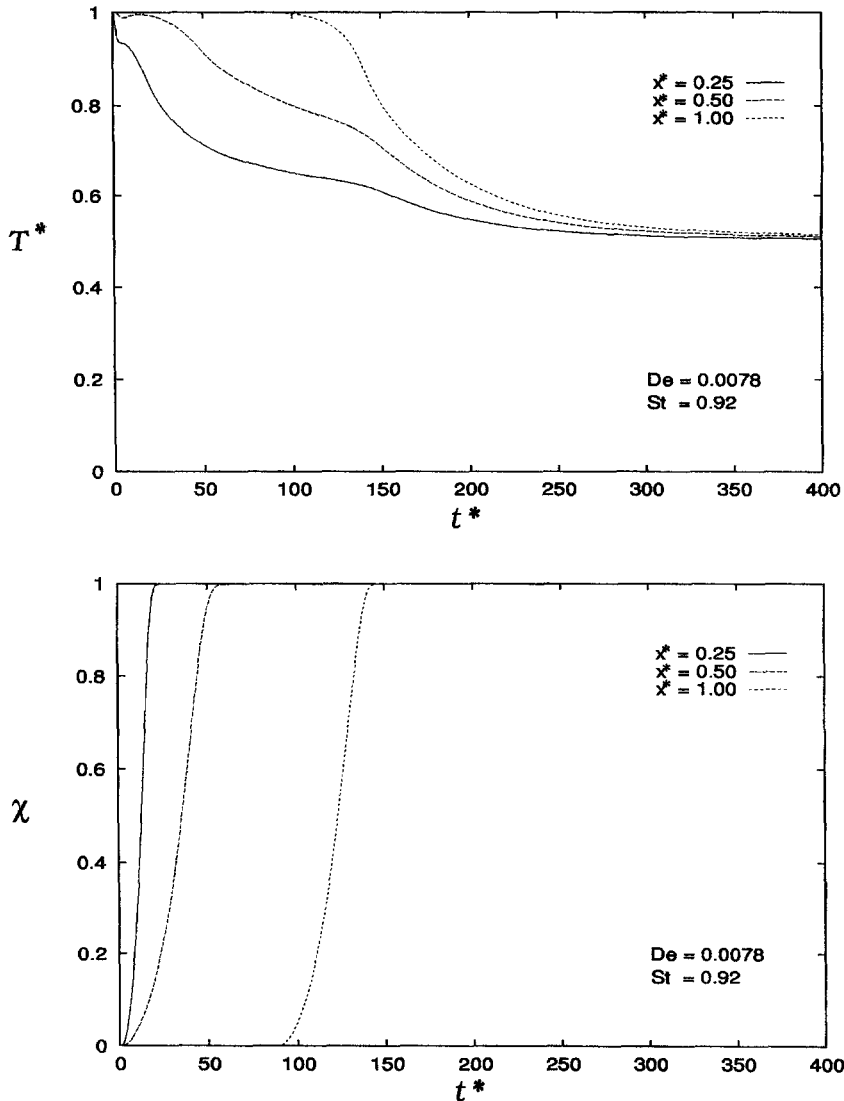


Fig. 9. Temperature (T^*) and crystallinity (χ) profiles during cooling computed for Nylon 6-6 using the coupled zone model.

9 for Nylon 6-6. The evolution of the temperature and the crystallinity is presented in Fig. 9 for points located at $x^* = 0.25$, $x^* = 0.5$ and $x^* = 1$ in the domain. A first significant change of slope is encountered in the temperature profile during the cooling process due to the considerable heat released during the passage of the crystallization front. A second change of slope occurs when the whole domain has crystallized and there is no more latent heat released due to the phase change process. These two phenomena are not exhibited by an uncoupled model.

CONCLUSION

The importance and the nature of the coupling between the crystallization kinetics of a polymeric material with the energy equation has been examined in this paper. By comparing the temperature and crys-

tallinity distributions obtained from a zone model with the Neumann's solution and the uncoupled heat diffusion equation, it is possible to identify four different regimes of coupling. Combinations of these numbers have revealed regimes where the coupling is strong or weak and conditions under which a sharp interface between solid and liquid zones is an acceptable approximation.

A front tracking method such as Stefan's approach is valid and easier to use at low values of De since a sharp interface introduces a singularity that requires more computations in the one-domain formulation used in the zone model. The series solution of the uncoupled heat diffusion equation is justifiable at low values of St . At low values of both St and De , temperature solutions are indistinguishable from the zone model. Outside these narrow regions, it is essential to use a zone model in which the crystallization kinetics

are coupled with the energy equation, otherwise significant errors in the crystallinity and the temperature profiles will be introduced. Examples of the cooling of semi-crystalline polymers were presented to illustrate the limitations of the Stefan's and uncoupled approaches and the utility of the zone model.

Acknowledgements—The financial support of the E. I. DuPont de Nemours & Company Inc. and the Delaware Research Partnership Program is gratefully acknowledged.

REFERENCES

1. M. N. Ozisik, *Heat Conduction*, p. 406. Wiley, New York (1980).
2. Z. Tadmor and C. G. Gogos, *Principles of Polymer Processing*, p. 293. Wiley, New York (1979).
3. J. Stefan, Ueber die theorie der eisbildung insbesondere ueber die eisbildung in polameere, *Ann. Phys. Chem.* **42**, 269–286 (1891).
4. F. Neumann, C. P. Frank and R. von Mises, *Die Differential und Integral Gleichungen der Mechanik und Physik*, Vol. 2. Vieweg, Braunschweig (1927).
5. H. Janeschitz-Kriegl, Changing view on the classical Stefan problem. In *One Hundred Years of Chemical Engineering* (Edited by N. A. Peppas), pp. 111–124. Kluwer, Boston (1989).
6. G. Eder, H. Janeschitz-Kriegl and S. Liedauer, Crystallization processes in quiescent and moving polymer melts under heat transfer conditions, *Prog. Polymer Sci.* **15**, 629–714 (1990).
7. G. Eder and H. Janeschitz-Kriegl, Stefan problem and polymer processing, *Polymer Bull.* **11**, 93–98 (1984).
8. G. Kroboth, S. Liedauer and H. Janeschitz-Kriegl, Crystallization fronts in quenched polymer samples, *Polymer Bull.* **14**, 1–8 (1985).
9. M. Erhun and S. G. Advani, A predictive model for heat flow during crystallization of semi-crystalline polymers, *J. Thermoplastic Compos. Mater.* **3**, 90–109 (1990).
10. J. Berger and W. Schneider, A zone model of rate controlled solidification, *Plastics Rubber Process. Appl.* **6**, 127–133 (1986).
11. G. Astarita and J. M. Kenny, The Stefan and Deborah numbers in polymer crystallization, *Chem. Engng Commun.* **53**, 69–84 (1987).
12. R. Ocone and G. Astarita, Continuous and discontinuous models for transport phenomena in polymers, *A.I.Ch.E. JI* **33**, 423–435 (1987).
13. J. Crank, *Free and Moving Boundary Problems*, p. 226. Clarendon Press, Oxford (1984).
14. A. Wasiak, Kinetics of polymer crystallization in non-isothermal conditions, *Macromolec. Chem.* **2**, 211–245 (1991).
15. W. D. Murray and F. Landis, Numerical and machine solutions of transient heat-conduction problems involving melting and freezing, *J. Heat Transfer* May, 106–112 (1959).
16. H. S. Carslaw and J. C. Jaeger, *Conduction of Heat in Solids* (2nd Edn). Clarendon Press, Oxford (1986).
17. A. Ziabicki, *Fundamentals of Fibre Formation*, p. 112. Wiley, New York (1976).
18. R. Pfluger, Physical constants of various polyamides. In *Polymer Handbook* (Edited by J. Brandrup and E. H. Immergut), p. 109. Wiley, New York (1989).