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THERMAL ANALYSIS OF THE OVERINJECTION OF A MOLTEN THERMOPLASTIC OVER A THERMOPLASTIC INSERT

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Ce mémoire intitulé:

THERMAL ANALYSIS OF THE OVERINJECTION OF A MOLTEN THERMOPLASTIC OVER A THERMOPLASTIC INSERT

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en vue de l'obtention du diplôme de: Maîtrise ès sciences appliquées

a été dûment accepté par le jury d'examen constitué de:

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To my parents with appreciation

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I would like to thank all of the people who helped to make this work possible. First of all special thanks to my director, Mr. R. Gauvin who made my higher education possible and helped me all the way to complete this work. Thanks are also due to department of metallurgy who made the necessary software and computer facilities accessible for me. Thanks to M. Richard, responsible of computer section of department of metallurgy who provided me the necessary information for using the work stations. Thanks are also due to Mr. H. Nguyen for his useful counsels. Finally, I would like to thank the members of jury who accepted to read this work and help me with their opinions.

RÉSUMÉ

L'objectif de cette recherche est d'étudier les fusion et solidification transitoires des interfaces solide-liquide et moule-liquide présents lors de l'injection d'un polymère fondu sur un insert thermoplastique solide. La solution d'un modèle mathématique préalablement défini a été obtenue à l'aide de la méthode des éléments finis.

Le but de la présente recherche est d'étudier l'effet des changements de certains paramètres sur cette profondeur fondue; pour atteindre ce but, la géométrie, les propriétés physiques des matières et les conditions initiales et frontières du problème doivent être spécifiées.

Les équations de transfert thermique correspondantes sont résolues dans le domaine du temps et de l'espace, par la méthode des éléments finis, à l'aide du logiciel ABAQUS. Le logiciel fournit l'historique thermique de différents points dans la pièce, et la position du front de changement de phase est calculée par la suite à partir de l'historique thermique, par une méthode d'approximation.

Malgré le fait que plusieurs types d'éléments peuvent être considérés pour modéliser la géométrie des problèmes de transfert thermique, les éléments linéaires sont souvent préférés

parce que les éléments d'ordres supérieurs n'apportent pas d'améliorations significatives des résultats. Un maillage monodimensionnel simple contenant une certaine quantité de "link elements" a été retenu pour la présente étude.

Le polystyrène (PS) et le polyéthylène teraphtalate (PET) ont été retenus pour représenter les cas amorphe et semi-cristallin. Les résultats ont été obtenus avec trois ensembles de température, pour chacune des deux matières. L'effet du rapport des épaisseurs solide et liquide initiales a également été considéré. Il est clairement apparu que la solution des équations de transfert de chaleur dépend principalement des conditions frontières.

Différents paramètres provoqent différents scénarios de fusion ou de solidification rapide. La procédure de transfert thermique peut évoluer de différentes manières dictées par les paramètres du système. La vitesse initiale du front de fusion peut être positive ou négative. Puisque les masses solide et fondue sont finies, il est possible d'obtenir une stabilité thermique à long terme; l'atteinte de cette situation dépend des paramètres thermiques du système. Plus la différence de température entre le moule et la masse fondue est élevée, plus profonde est la pénétration du front dans l'insert solide. La position limite du front est aussi contrôlée par le rapport initial des épaisseurs du liquide et du solide. Si la zone liquide est relativement importante, le corps froid fond complètement avant que l'ensemble ne soit refroidi. Le résultat exact dépend du polymère choisi.

Il n'y a pas de solution exacte au problème traité dans ce travail. La cinétique de la solidification du polymère fondu au voisinage des parois du moule est analogue, lors des étapes initiales, à celle obtenue analytiquement par Stéfan pour le milieu semi-infini; les résultats de la solution numérique développée ici se comparent bien à ceux-ci.

ABSTRACT

The transient melting and solidification layer generated by the injection of a thermoplastic melt over a thermoplastic insert, at mold-melt interface and melt-solid insert interface, is investigated by using finite element techniques. The problem presents considerable computational difficulties due to the moving interface and the nature of the solutions in the solid and liquid regions. A mathematical model which is the basis of the finite element analysis is introduced. This mathematical model includes the geometry of the problem , differential equations , initial and boundary conditions. A one dimensional mesh is used to investigate the position of moving boundaries at different times. The position of the interfaces are calculated from the temperature history obtained from finite element analysis by the method available in literature.

To do the numerical computation , a finite element software, ABAQUS is used, the program is written to investigate the process for two kinds of thermoplastics., Amorphous and crystalline. Polystyrene (PS) and Polyethylene tertraphtalate (PET) are chosen to represent these two groups of polymers. Non-dimensional heat transfer equations are solved for the amorphous Polystyrene, while taking the change of thermophysical properties with temperature into account. For PET the problem is more simplified by eliminating the change of these properties with temperature.

There is no exact solution for the problem, and numerical solution has not been studied for this special problem. In the case of PET, however, numerical solutions are tested for accuracy by comparing them with analytical solutions to classical problems at short times. The agreement is good at short times while for longer times the difference between the analytical result and numerical approximation is more sensible, which is due to the different natures of the problems.

Different parameter regimes induced possible scenarios of rapid initial thawing or freezing and the freeze front may then grow or decay to a limiting value as a steady state develops. The physical and mathematical consequences of altering certain parameters is investigated and the results are discussed in detail. The emphasize has been on the process parameters like temperature system including mold, melt and insert temperature and different thickness ratio of solid and melt polymer.

For different temperature systems, the initial motion of the melt-solid interface remains the same, while large time steady state solution varies according to the thermal parameters of the system. In the case of melting of the solid insert a limiting position of melt-solid interface can be detected which depends on the mold temperature. The higher the temperature difference between the mold and the melt, the lower is the penetration depth of the front in the solid insert. The limiting position of the front also can be controlled by initial thickness ratio of melt-solid polymer. If the liquid region is relatively large the process may be terminated when the cold body melts completely leaving purely liquid. The exact condition depends on the specific polymer under consideration.

CONDENSÉ EN FRANÇAIS

L'objectif de cette recherche est d'étudier les fusion et solidification transitoires des interfaces solide-liquide et moule-liquide présents lors de l'injection d'un polymère fondu sur un insert thermoplastique solide. La solution d'un modèle mathématique préalablement défini a été obtenue à l'aide de la méthode des éléments finis. La connaissance de la distribution des températures dans le solide et le liquide, des taux de refroidissement locaux et des gradients de température à chaque instant revêt une grande importance puisque ces informations permettent de conclure quant à l'interpénétration de la frontière solide-liquide, et aussi d'évaluer la qualité du joint après solidification.

Le modèle mathématique proposé permet de quantifier les effets des changements des paramètres du procédé. La modélisation numérique prend tout son sens au vu des coûts et délais impliqués par une étude expérimentale de ces changements.

Le procédé d'injection d'un thermoplastique fondu sur un insert thermoplastique est semblable à la soudure ou au "dip-coating" des polymères. Pour obtenir un lien fort et uniforme entre la partie fondue et l'insert, ce dernier doit fondre jusqu'à une certaine profondeur. Le but de la présente recherche est d'étudier l'effet des changements de certains paramètres sur cette profondeur fondue; pour atteindre ce but, la géométrie, les propriétés physiques des matières et les conditions initiales et frontières du problème doivent être spécifiées.

Les équations de transfert thermique correspondantes sont résolues dans le domaine du temps et de l'espace, par la méthode des éléments finis, à l'aide du logiciel ABAQUS. Le logiciel fournit l'historique thermique de différents points dans la pièce, et la position du front de changement de phase est calculée par la suite à partir de l'historique thermique, par une méthode d'approximation.

Les problèmes de transfert de chaleur avec changements de phase présentent la caractéristique particulière d'un interface entre les phases solide et liquide, dans laquelle la chaleur "latente" associée au changement de phase est absorbée et libérée. La position de cet interface change continuellement dans le temps. En conséquence, les solutions de ces problèmes transitoires dits "à frontière mobile" ou "problèmes de Stéfan" sont difficiles à obtenir. La localisation et le déplacement de l'interface solide-liquide sont à priori des inconnues du problème.

Les équations différentielles définissant le problème à frontière mobile sont paraboliques, soit d'ordre 2 par rapport au temps. Les équations de la conduction en régime transitoire pour le solide et le liquide sont liées par les conditions à l'interface. Les solutions analytiques exactes des problèmes de ce type ont été obtenues par Stefan dans le cadre de son étude sur la formation de la glace. Ces solutions ne sont toutefois utilisables que dans certaines situations idéales, pour des régions infinies ou semi-infinies, avec des conditions frontières et initiales très simples. La solution de problèmes plus généraux de changement de phase a été discutée par Neuman; hormis certains cas idéaux, presque toutes les situations requièrent l'utilisation de techniques numériques.

Différentes méthodes numériques peuvent être appliquées au calcul des problèmes de solidification. Les méthodes de différences finies ont été traditionellement utilisées, mais les méthodes d'éléments finis ont gagné beaucoup de terrain au cours de la dernière décénie pour la solution de ces problèmes. Ces dernières présentent les avantages d'une meilleure adapatabilité aux géométries complexes, d'une facilité d'implantation des conditions frontières, et d'une plus grande précision des résultats.

La quantité de chaleur latente libérée peut être présentée de différentes façons, essentiellement regroupables sous 2 catégories, soit les méthodes du "front-tracking" et les méthodes d'enthalpie. Ces dernières, utilisées pour la présente étude, donnent la localisation du front de changement de phase à partir des températures calculées. Elles sont facilement utilisables avec les logiciels existants, et permettent une présentation simple de la chaleur libérée à l'interface, dont la position n'a pas à être spécifiée à priori.

Malgré le fait que plusieurs types d'éléments peuvent être considérés pour modéliser la géométrie des problèmes de transfert thermique, les éléments linéaires sont souvent préférés parce que les éléments d'ordres supérieurs n'apportent pas d'améliorations significatives des résultats. Un maillage monodimensionnel simple contenant une certaine quantité de "link elements" a été retenu pour la présente étude.

Dans le cas où le changement de phase a lieu à une température spécifique, une portée de température, sur laquelle a lieu ce changement, doit être choisie. Notons qu'une faible portée est préférable puisqu'elle permet une meilleure représentation du problème concret. La portée doit ensuite être combinée à un intervalle de temps approprié à l'obtention d'une bonne approximation. Cet intervalle est choisi de façon à ce que le changement de température maximal y correspondant soit inférieur à la portée.

Tel que mentionné précédemment, la position de l'interface est calculée à partir des résultats de l'historique thermique. La méthode suggérée par Voller et Cross a été utilisée pour la présente recherche.

Les températures de transition des polymères sont relativement élevées; les quantités de chaleur requises pour leur fusion sont grandes, et les taux de transfert thermique sont limités par la conductivité et la stabilité thermique de la matière. L'ensemble de ces propriétés rend possible la situation dans laquelle la décomposition ou la combustion du polymère près des sources de chaleur a lieu avant qu'une quantité de chaleur suffisante n'ait pû permettre la fusion souhaitée de la masse. Les excellentes propriétés isolantes des polymères solides et fondus permettent de retenir la conduction et la diffusion comme modes de transfert de chaleur en écoulement laminaire; la viscosité élevée des polymères fondus limite fortement la convection dans ces systèmes.

Règle générale, les polymères amorphes et cristallins ont des comportements différents en transfert thermique; ces derniers évacuent une quantité de chaleur latente lors de leur solidification, contrairement aux premiers. Plusieurs polymères présentent une morphologie solide cristalline; leur température de fusion peut être définie comme celle à laquelle les entités cristallines perdent leur cohésion. Il en va autrement des polymères amorphes, pour lesquels la température la plus importante Tg est définie lorsque le comportement passe de caoutchouteux à vitreux. La plupart des polymères thermoplastiques sont semi-cristallins; les quantités thermodynamiques prennent alors des valeurs intermédiaires à celles correspondant aux régions purement cristallines et amorphes. Ces propriétés sont fortement dépendantes de la densité, du poids, de l'orientation moléculaire, et d'autres facteurs.

Le polystyrène (PS) et le polyéthylène teraphtalate (PET) ont été retenus pour représenter les cas amorphe et semi-cristallin; les propriétés requises ont été tirées de la littérature. L'influence de la température sur ces propriétés a été considérée pour le PS, mais pour le PET le problème devient plus général si ces effets sont négligés. Les résultats ont été obtenus avec trois ensembles de température, pour chacune des deux matières. L'effet du rapport des épaisseurs solide et liquide initiales a également été considéré. Il est clairement apparu que la solution des équations de transfert de chaleur dépend principalement des conditions frontières.

Différents paramètres provoqent différents scénarios de fusion ou de solidification rapide. La procédure de transfert thermique peut évoluer de différentes manières dictées par les paramètres du système. La vitesse initiale du front de fusion peut être positive ou négative. Puisque les masses solide et fondue sont finies, il est possible d'obtenir une stabilité thermique à long terme; l'atteinte de cette situation dépend des paramètres thermiques du système.

Dans le cas du PS, l'insert solide fond et la position limite de l'interface solide-liquide est fonction de la température du moule. Plus la différence de température entre le moule et la masse fondue est élevée, plus profonde est la pénétration du front dans l'insert solide. La position limite du front est aussi contrôlée par le rapport initial des épaisseurs du liquide et du solide. Si la zone liquide est relativement importante, le corps froid fond complètement avant que l'ensemble ne soit refroidi. Le résultat exact dépend du polymère choisi.

Avec le PET, la solidification s'amorce des deux côtés à la fois. Les interfaces moule-matière fondue et insert-matière fondue se déplacent l'un vers l'autre, l'état stationnaire correspondant à la solidification complète de la matière.

Il n'y a pas de solution exacte au problème traité dans ce travail. La cinétique de la solidification du polymère fondu au voisinage des parois du moule est analogue, lors des étapes initiales, à celle obtenue analytiquement par Stéfan pour le milieu semi-infini; les résultats de la solution numérique développée ici se comparent bien à ceux-ci. Les deux solutions divergent significativement avec le temps, témoignant de la nature différente des deux problèmes.

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LIST OF SYMBOLS

c : Specific heat

c_1 : Specific heat of solid

c_2 : Specific heat of liquid

C : Heat Capacity

$\mathbf{C}$: Capacitance matrix

c_{ij} : Members of capacitance matrix

c_m : Specific heat at melting range

c^* : Effective heat capacity

$\mathbf{F}$: Thermal loading matrix

f_i : Members of thermal loading term matrix

h : Heat convection coefficient

H_s : Enthalpy of solid phase

H_l : Enthalpy of liquid phase

H_i : Enthalpy values at the nodes

ΔH_m : Enthalpy of fusion

i : 1 or 2 referring to solid or liquid regions respectively

k : Thermal conductivity

$\mathbf{K}$: Thermal conductivity matrix

k_{ij} : Members of conductance matrix

k_l : Thermal conductivity of liquid phase

k_s : Thermal conductivity of solid phase

L : Latent heat of fusion

N : Number of elements

N_i : Basis or shape functions

$\hat{n}$: Unit outward normal

n : Time increment number

q : Heat transfer rate

S : Phase change interface

s^* : Fraction of element which is solid

T : Temperature

$\mathbf{T}$: The vector of unknown nodal temperatures

$\hat{T}$: Known boundary temperature

T_0 : Initial temperature

T_g : Glass transition temperature

T_i : Nodal temperature

T_{il} : Initial temperature of liquid

T_{is} : Initial temperature of solid

T_l : Upper limit of melting range

T_s : Lower limit of melting range

T_m : Phase change temperature

$T_l(x,t)$: Liquidus temperature as a function of time and space

$T_s(x,t)$: Solidus temperature as a function of time and space

T_{ref} : Reference temperature

t : Time

δt, Δt : Length of time increment

U : Internal energy

X : The ratio of initial thickness of melt to initial thickness of solid

δx : Element length

α_1 & α_2 : Coefficients of linear approximation for temperature distributi
in an element

ε : Half of the melting range

ρ : Density

τ : Time limit

Ω : Domain of the problem

Ω_e : Domain of an element

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INTRODUCTION

Over the past years many authors have been preoccupied with the numerical solution of phase change problems. Interests lie in the field of ground freezing problems, solar energy application or, as in our case, the phase change of materials in the mold.

The knowledge of the locations of liquids and solids temperatures, the temperature at any point within the material in the mold, the local cooling rate, the temperature gradient at all appropriate time intervals is of great importance, since with this information we can draw conclusions concerning the likelihood of formation of voids and cracks and certain microstructures and if necessary adjust the design parameters to improve the quality of the molded part. Mathematical model of melting (solidification) processes are used to isolate and identify the effects of changes in individual variables, such changes can be difficult to make in an experiment and modeling is a good way to study these variations.

In this work the process of injection of a molten thermoplastic over a solid thermoplastic insert is studied. The process is similar in concept to welding or dip coating of polymers. In order to obtain a strong and uniform bound between the molded part and its insert, the solid insert surface must melt to a certain depth. In this work, we model the process of phase change at the interface between melt and solid. The resulting heat transfer process may progress in many different ways dictated by the parameters involved in the system. In the way to reach steady state heat transfer condition, the melt-solid interface moves to a certain depth before the two portions begin to solidify together and join as a single piece.

The objective of this study is to correlate with other process parameters, the depth of melt in the solid insert, to study the heat transfer at the melt-solid interface in order to demonstrate how the physical properties of polymers and different system characteristics affect the final results. To reach this goal a model is introduced. The simulation proceed by specifying the geometry, material properties, boundary and initial conditions for the process. The corresponding heat transfer equations are solved, in time and space, by finite element method, using ABAQUS, to determine the thermal history at various location in the part. Then the phase change position is calculated by an approximation method from temperature history results.

A characteristic of heat transfer problems dealing with phase change is the existence of an interface separating the phases. On this interface, the latent heat associated with the phase change is absorbed or liberated and as a consequence of heat transfer processes in the two phases, the location of the interface is continuously changing in time. Transient heat transfer problems involving melting or solidification are generally called 'phase change' or 'moving -boundary' problems. The solution of such problems is inherently difficult because the interface between the solid and liquid phases is moving. As a result the location of the solid-liquid interface is not known a priori and must follow as a part of the solution. Also the way in which this surface moves has to be determined.

For a phase-change problem, the mathematical formulation consists of parabolic non-linear differential equation governing the conduction of heat through a medium, coupled with appropriate boundary conditions. Early analytic works on the solution of phase change problems include those by Stefan in relation to the ice formation. The exact solution of a more general phase change problem, however, was discussed by Neuman. The exact solutions of phase-change problems are limited to a number of idealized situations involving semi-infinite or infinite regions and subjected to simple boundary and initial conditions and in a case of complex geometry or complicated boundary conditions, they are not applicable. Therefore for practical purposes, apart from the few exact solutions, all problems have to be attacked by numerical methods.

Various numerical techniques can be applied for the computation of solidification problems, traditionally the finite difference method has been used, but the last ten years have shown an increasing tendency to apply the finite element method to heat conduction analysis. The reason for this is the ability of this method to handle complex geometry, the ease in implementing boundary conditions and the capacity it has as a flexible purpose technique, since the method is completely general, the temperature and heat flux boundary condition may be specified at any point and desired accuracy may be obtained.

The latent heat release can be presented by two methods , front-tracking and enthalpy method . The enthalpy method is used in this study in which the phase change front is not simultaneously tracked but derived afterwards from calculated temperature. This method has the advantage of ease of implementation in existing program packages, of simple representation of latent heat release at the interface, the position of which need not to be specified a priori, of capability of dealing with 'mushy' phase change problems or complicated shapes and proven convergence to the weak solution of the differential equation. A geometry can be represented by a combination of different finite elements. Most of the proposed elements that have been used in the stress analysis of solids are applicable. However for transient phase change problem, usually linear elements are used.

Polystyrene(PS) and Polyethylene Tetraphtalate(PET) are chosen to represent amorphous and semi-crystalline polymers. The change of thermal properties like thermal conductivity and heat capacity with temperature is calculated according to the formulation in the literature. For this case the change of thermophysical properties with temperature is accounted for in the calculation, although the change of these properties with temperature is small and usually can be neglected.

No doubt, there are different processing parameters and operating conditions, that control the advance of melt interface in the solid (or the advance of solid in the melt) until a specific point, but a crucial component in simulating solidification (or melting) in the mold is the handling of heat transfer at the interface between the mold and the material, The solution of the equations depends on the selection of boundary conditions.

As we can see from the results the solution to the heat transfer equations is largely controlled by the boundary conditions used to specify the problem. The initial velocity of melt front may have negative or positive influence on the melting or freezing. In the case of melting of the solid insert, a limiting position of melt-solid interface can be detected. This limiting position depends on the mold temperature. For long times the temperature difference between melt and mold wall controls the heat transfer rate of the system.

Although there is no exact analytical solution for this problem, for short times, numerical solutions were tested for accuracy by comparing them to analytical solution to classical problems. This would have revealed any programming errors.

Chapter 1

Heat Transfer During Phase Change

1.1 Introduction

A characteristic of heat transfer problems dealing with phase change is the existence of an interface separating the phases. On this interface, the latent heat associated with the phase change is absorbed or liberated and as a consequence of heat transfer processes in the two phases, the location of the interface is continuously changing in time. Transient heat transfer problems involving melting or solidification are generally called 'phase change' or 'moving -boundary' problems. The first published discussion of such problems seems to be the one by Stefan in 1889, and for this reason the problem is frequently referred to as the problem of Stefan. The solution of such problems is inherently difficult because the interface between the solid and liquid phases is moving. As a result the location of the solid-liquid interface is not known a priori and must follow as a part of the solution. Also the way in which this surface moves has to be determined.

In the solidification of pure substances, like water, the solidification takes place at a discrete temperature and the solid-liquid phases are separated by a sharp moving interface. On the other hand in the solidification (or melting) of mixtures (alloys) and impure materials the solidification takes place over an extended temperature range and as a result the solid and liquid phases are separated by a two-phase moving region (Özisik, 1993).

This literature review for heat transfer aspect of the problem, concerns the general mathematical formulation which defines the problem and different available solutions.

1.2 Mathematical Formulation

When a temperature gradient exist in a body, there is an energy transfer from the high-temperature region to the low-temperature region, so the heat is transferred by conduction and the heat transfer equation is governed by Fourier law of heat conduction. If the system is in a steady state which means that the temperature does not change with time, then the problem is a simple one and we need only to substitute the appropriate values in Fourier's equation and solve for desired value. However, if the temperature of the solid is changing with time, or if there are heat sources or sinks within the solid, the situation is more complex. The unsteady state differential equation for heat transfer in this case is obtained by balancing the energy for an element inside the body (Holman 1981).

For a phase-change problem, the mathematical formulation consists of the differential equation governing the conduction of heat through a medium, coupled with appropriate boundary conditions. For a moving boundary problem the equation is of parabolic type which means that differential equations contain first order time derivatives (Crank, 1984). The form of boundary condition is usually of two types, Dirichlet (known temperature) or Neuman (known heat flux), or can be a mixture of two. Since we are dealing with transient problem we must also specify the initial state, or temperature distribution at the initial condition. The situations involving a change of phase, the classical Stefan problem, is used to describe the conduction in a domain including two separate phases, Figure 1.1. Thus on the subdomain $\Omega 1$, $\Omega 2$ we have ($\Omega 1 \cup \Omega 2 = \Omega$) (Lewis & Roberts, 1987) :

$$\nabla.(k_i \nabla T_i) = \rho_i c_i \dot{T}_i; \qquad (x,t) \in \Omega_i \times [0,\tau] \qquad [1]$$

$$T_i(x,t) = \hat{T}(x).f(t); \qquad (x,t) \in G_{1i} \times [0,\tau] \qquad [2]$$

$$k_i \nabla T_i.\hat{n} + q_i + h_i(T_i - T_{ai}) = 0; \qquad (x,t) \in G_{2i} \times [0,\tau] \qquad [3]$$

$$T_i(x,0) = T_{0i}(x); \qquad x \in \Omega_i \qquad [4]$$

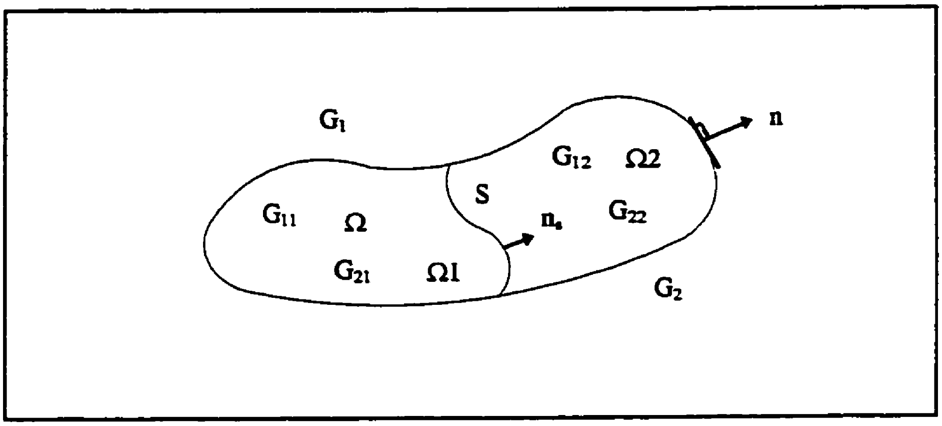

Figure 1.1: Domain of phase change

K = thermal conductivity

T = temperature

ρ = density

C = heat capacity

T = time

τ = time limit

T = known boundary temperature

T_0 = initial temperature

$\hat{n}$ = unit outward normal

H = heat convection coefficient

I = 1 or 2 referring to solid or liquid regions respectively

Equation [1] refers to transient thermal fields in a substance with temperature dependent thermophysical properties. For the solution of Stefan problems two equation of the form of equation [1] must be solved, one for the solid and one for the liquid phase. Besides the initial conditions and conditions imposed at the boundary of the domain, the following conditions must be satisfied at the solidification front;

$$k_1 \nabla T_1 . \hat{n}_s - k_2 \nabla T_2 . \hat{n}_s = \rho L \dot{S} \qquad [5]$$

ρ = density

K_1 = thermal conductivity of solid

K_2 = thermal conductivity of melt

T_1 = solid temperature

T_2 = melt temperature

$\hat{n}_s$ = unit outward normal at interface

L = latent heat

S = phase change interface

This equation is obtained by considering the energy balance at the interface (Carslaw and Jaeger, 1984). The transient heat conduction equations for solid and liquid domain are coupled by this boundary condition at the interface. The interface boundary conditions given by [5] is nonlinear because if we relate ds(t)/dt to the derivative of temperatures this equation leads to a non-linear differential equation for temperature (Özisik, 1993).

Usually, the generalized form of this problem incorporate any or all of the following non-linear features (Crank, 1984);

- The heat parameters K_i, c_i, ρ_i may all be functions of T,x,t.
- On the moving interface the temperature T may be space and time dependent.
- There may be a heat source or sink on the moving boundary.

1.3 Changes in Thermophysical Properties During the Phase Change

From thermodynamic point of view phase transition are typical first-order transitions in which a primary thermodynamic function, such as enthalpy shows sudden jump. This sudden change in enthalpy is due to the energy absorption required to change the phase at a given temperature. For a glassy material however, phase change is a thermodynamic second order transition in which a plot of a primary quantity shows an abrupt change in slope, while a plot of a secondary quantity, like specific heat, shows a sudden jump.

1.4 Different Methods for Solution of Phase-Change Problems

The fundamental feature of this type of problem is that the location of the boundary is both unknown and moving, and that the parabolic heat conduction equation is to be solved in a region whose boundary is also to be determined.

Early analytic works on the solution of phase change problems include those by Stefan in relation to the ice formation. The exact solution of a more general phase change problem, however, was discussed by Neuman in his lectures in 1912. The exact solutions of phase-change problems are limited to a number of idealized situations involving semi-infinite or infinite regions and subjected to simple boundary and initial conditions.. Carslaw and Jaeger(1984) give a very good review of available analytical and semi-analytical solutions available for phase-change problems with different geometry and simple boundary conditions.

In the Stefan problem, since two heat equation coupled by the boundary conditions, which amounts to the solution of non-linear problem(Özisik,1993; Carslaw and Jaeger, 1984), few analytical solution method exist. In a case of complex geometry or complicated boundary conditions, the superposition principal is not applicable and each case must be treated separately. Therefore for practical purposes, apart from the few exact solutions, all problems have to be attacked by numerical methods. But even then care must be taken in choice of proper solution method.

1.5 Numerical Methods

Although the solution process is now well established for linear problems involving multidimensional geometry and time dependent boundary conditions, the complexities of problems involving change of phase have not yet been fully analyzed. When the phase change takes place over a wide range of temperatures the computational problems with the representation of latent heat effects are easily overcome, however a zero width phase change interval is more difficult to deal with computationally (Comini et al, 1974; Grifit & Nassersharif, 1990; Morgan, Lewis & Zienkiewicz, 1978; Tamma & Namburu, 1990; Voller & Cross, 1983), therefore the zero width interval is in practice often approximated by a narrow temperature range which facilitates incorporation of latent heat affects.

The systematic use of numerical methods has the advantages that the variation in the thermal properties with temperature which can be considerable over the ranges of temperature involved in problems on melting and solidification can be taken into account. Various numerical techniques can be applied for the computation of solidification problems (Carslaw & Jaeger, 1959; Crank, 1984), traditionally the finite difference method has been used, but the last ten years have shown an increasing tendency to apply the finite element method to heat conduction analysis. The reason for this is the ability of this method to handle complex geometry, the ease in implementing boundary conditions and the capacity it has as a flexible purpose technique, since the method is completely general, the temperature and heat flux boundary condition may be specified at any point and desired accuracy may be obtained.

1.5.1 Finite Element Techniques for Phase-Change Problems.

The latent heat released can be presented in many different ways but numerical techniques involving finite elements can be separated in two distinct groups based on the formulation of the problem;

- The front-tracking methods in which the phase change front is tracked continuously and the latent heat is treated as a moving boundary condition. Here the energy equation is written in terms of temperature as the dependent variable and involves the technique of moving or deforming elements (Criveilli & Idelsohn, 1986; Rubinsky & Cravahlo; 1981; Yoo & Rubinsky, 1983). This requires either deforming or alternating grids, transformation of variables or coordinates (Bell Wedgewood, 1993), introduction of special algorithms near the phase change interface or choosing the time step so that the interface coincides with grid nodes (Voller & Cross, 1980).

- Amore general method is the enthalpy method, in which the enthalpy is the dependent variable (Comini & Guidice, 1974; Goodrich, 1977; Tamma & Namburu, 1990). In this method, the phase change front is not simultaneously tracked but derived afterwards from the calculated temperatures. This is possible because the phase front conditions are implicity accounted for in the enthalpy definition. This method has the advantage of ease of implementation in existing program packages, of simple representation of latent heat release at the interface, the position of which need not to be specified a priori, of capability of dealing with 'mushy' phase change problems or complicated shapes and proven convergence to the weak solution of the differential equation (Bell, 1982).

The temperature based formulation suffers from effectively handling abrupt variations in heat capacity and approaches to approximate this in the phase change zone. The implementations in this method are troublesome and often complicated equations must be solved. Enthalpy methods seem more natural in eliminating some of these problems but do experience some of the same difficulties. Numerical difficulties are either in accurately representing the temperature history, locating the phase front or both (Bell, 1982; Voller & Cross, 1982).

1.6 Enthalpy Method for Solution of Phase-Change Problems

A more general method is the enthalpy method in which the phase change boundary is not simultaneously tracked but derived from calculated temperatures. Enthalpy method is a fixed-grid method, in which the interface position is generally at an unknown location between nodes and the latent heat evolution is treated in terms of a temperature-dependent specific heat. This general formulation does not take separate account of the latent heat effect accompanying a change of phase but approximated to it by allowing rapid variation in the heat capacity. This is possible because the phase front conditions are simply accounted for in the enthalpy equation.

The advantages of the enthalpy method is that a single energy equation becomes applicable in both phases, hence there is no need to consider liquid and solid phases separately. Therefore any numerical scheme such as the finite-difference or finite element method can readily be adopted for the solution. In addition, the enthalpy method is applicable for the solution of phase-change problems involving both, a distinct phase change at a discrete temperature as well as phase change taking place over an extended range of temperatures. But it should be mentioned that although the enthalpy method can be applied to isothermal freezing problems and the predicted temperature distribution in such cases are reasonable, the predicted time history of a typical point usually displays a pronounced step like behavior as a consequence of the enforced temperature plateau, about the phase change temperature. This behavior can be smoothed by;

1- reducing the spatial step size

2- introducing a special algorithm in the neighborhood of the phase change to effectively track the moving interface.

3- by spreading the phase change over a temperature range

4- by combination of these methods.

1.6.1 Enthalpy Formulation of Phase-Change Problems

Figures 1-2a and 1-2b shows enthalpy-temperature relations for a pure crystalline substances and eutectics and a glassy substance or alloy. For pure substances the phase change takes place at a discrete temperature, and hence is associated with the latent heat L. Therefore in figure 1.2a a jump discontinuity occurs at the melting temperature T_m. Hence $\partial H/\partial T$ becomes infinite and the energy equation apparently is not meaningful at this point, however it has been shown that the enthalpy form of the energy equation given by;

$$\nabla.(k\nabla T)=\rho\frac{\partial H(T)}{\partial t} \qquad [6]$$

is equivalent to the usual temperature form in which the heat conduction equation is written separately for the liquid and solid regions and coupled with the energy balance equation at the solid-liquid interface. Figure 1.2b shows that for alloys and glassy substances there is no single melting point temperature T_m because the phase change takes place over an extended temperature range from T_s to T_l, and a mushy zone exists between the all solid and all liquid regions. In the case of pure substances having a single melting point Tm, figure 1.2a, when the substance is in solid form at temperature T, the

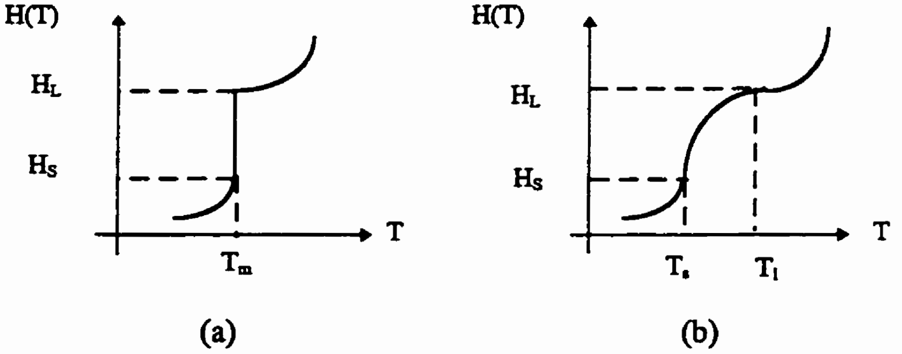

Figure 1.2: Enthalpy-Temperature relationship for (a) pure crystalline substances and (b) glassy substances or alloys

contains a sensible heat per unit mass $C_p(T-T_m)$, where the melting point temperature T_m is taken as the reference temperature. In liquid form, it contains latent heat L per unit mass in addition to the sensible heat, that is, $C_p(T-T_m)+L$. For the specific case considered here, the enthalpy is related to temperature by;

$$H=\begin{cases} C_P(T-T_m) & \textit{for} \quad T<T_m \\ C_P(T-T_m)+L & \textit{for} \quad T>T_m \end{cases} \qquad [7]$$

In the case of glassy substances or alloys such relationship between H(T) and T is obtained from either experimental data or standard physical data tables. In general, enthalpy is a nonlinear function of temperature. Therefore an enthalpy versus temperature variation must be available. Assuming linear release of latent heat over the mushy region, the variation of H(T) with temperature can be taken as;

$$H = \begin{cases} C_p T & \text{for} \quad T < T_s \quad \text{solid region} \\ C_p T + \dfrac{T - T_s}{T_l - T_s} L & \text{for} \quad T_s \le T \le T_l \quad \text{mushy region} \\ C_p T + L & \text{for} \quad T > T_l \quad \text{liquid region} \end{cases} \qquad [8]$$

The general form of enthalpy formulation for Stefan problem can be defined as follow;

$$H = \int_{T_{ref}}^{T} \rho c_1(T)\, dT \qquad \text{for} \qquad T < T_m \qquad [11]$$

$$H = \int_{T_{ref}}^{T_m} \rho c_1(T)\, dT + \rho L + \int_{T_m}^{T} \rho c_2(T)\, dT \qquad \text{for} \qquad T \ge T_m \qquad [12]$$

T_m = phase change temperature

T_{ref} = reference temperature

c_1 = specific heat of solid

c_2 =specific heat of liquid

L = latent heat

ρ = density

In case of a finite freezing interval $[T_s, T_l]$, the enthalpy can be found from;

$$H = \int_{T_{ref}}^{T} \rho c_1(T)\, dT \qquad for \qquad T < T_s \qquad [13]$$

$$H = \int_{T_{ref}}^{T_s} \rho c_1(T)\, dT + \int_{T_s}^{T} (\rho(dL/dT) + \rho c_m(T))\, dT \qquad for \qquad [T_s, T_l] \qquad [14]$$

$$H = \int_{T_{ref}}^{T_s} \rho c_1(T)\, dT + \rho L + \int_{T_s}^{T_l} \rho c_m(T)\, dT + \int_{T_l}^{T} \rho c_2(T)\, dT \qquad for \qquad T > T_l \qquad [15]$$

$T_s = T_m - \Delta T_m$ = solidus temperature

$T_l = T_m + \Delta T_m$ = liquidus temperature

c_m = specific heat at melting range

Since H is a unique function of temperature equation [6] can be written as follows;

$$[\frac{dH}{dT}][\frac{\partial T}{\partial t}] - \nabla.(k\nabla T) = 0 \qquad [16]$$

Now effective heat capacity which accounts for the latent heat evolution can be defined as; figure 1.3

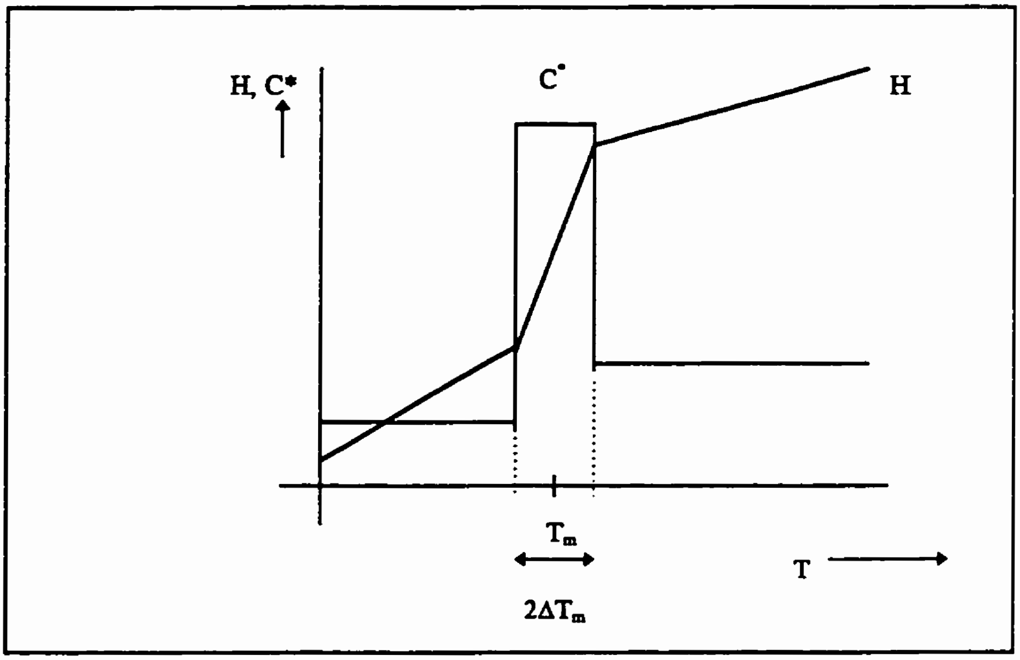

Figure 1.3: Typical plot of H and C*=dh/dt against temperature

$$c^{*} = \frac{dH}{dT} \qquad [17]$$

Materials with a discrete solidification temperature exhibit step changes in k and H at the solidification point which often cannot be handled easily in the numerical solution of the differential equations (Voller et al,1981, 1983, Morgan et al, 1978). Directly evaluating the effective heat capacity gives ;

$$\begin{aligned} c^{*} &= \rho c_1 && for \quad T < T_s \\ c^{*} &= \rho c_m + \frac{L}{T_l - T_s} && for \quad T_s \le T \le T_l \\ c^{*} &= \rho c_2 && for \quad T > T_l \end{aligned} \qquad [18]$$

where the latent heat release is assumed to take place homogeneously over the freezing range (Bonacina et al, 1973).

In the case of a Stefan problem, where the phase change occurs in a single melting point, this direct evaluation requires spreading of the phase change temperature across a temperature interval and thus introducing a freezing range. In this case, the freezing range must be kept small, to avoid too large deviations from the original solidification problem.

1.7 Finite Element Simulation of Solidification Problem

1.7.1 Theoretical Development

In strict mathematical sense, the case studied here is a transient one dimensional heat transfer problem. In fact this is a two dimensional problem, since there are two independent variables, x and t. However within the context of a finite element analysis, it is appropriate to refer to it as a one dimensional problem since only the spatial variable, x will be treated by finite element. Thus the Galerkin integral and integration by parts are done in the usual manner with respect to x. The variable t, for the most part is merely carried along during the following six step of the finite element process (Burnet 1987);

1- Writing the Galerkin residual equation for a typical element.

2- Integration by parts.

3- Substituting the general form of the element trial solution into interior integral in residual equations.

4- Developing specific expressions for the shape functions.

5- Substituting the shape functions into element equations and transform the integral into a form appropriate for numerical evaluations.

6- Preparing the expressions for the flux, using the trial functions.

1.7.2 Spatial Discritization

The finite element method has been chosen to descretize the domain Ω in space. The application of this method to the heat conduction equation is well documented, therefore only a brief description is warranted here.

The domain Ω is divided up into distinct regions or elements Ω_e such that,

$$\bigcup_{e=1}^{N} \Omega_e = \Omega \qquad [14]$$

Nodal points are then distributed at element vertices, along the element edges, and possibly in the element interior. We approximate temperature distribution by a weighted series of locally supported polynomial functions. The weights/amplitudes corresponds to the temperatures at the nodal points or nodes. Thus we have the approximation;

$$T(x,t) = \sum_{i=1}^{N} N_i(x) T_i(t) \qquad [20]$$

N_i = the basis or shape functions

T_i =nodal temperatures

N = number of elements

This is the classic 'separation of variable' technique sometimes also referred to as the method of Kantorovich, it means that numerical values of T_i may vary from one instant to another. The finite element procedure will transform the initial boundary value problems into a pure initial value problems. The latter will be solved by time stepping technique.

Substituting this approximation into the Galerkin weighted residual form of the differential equation, We obtain the semi-discrete system;

$$C\dot{T} + KT = F \qquad [21]$$

where T is the vector {T_i} of unknown nodal temperatures. The capacitance matrix C, the conductance matrix K and the thermal loading term F are defined as follows;

$$c_{ij} = \int_\Omega \frac{dH}{dT} N_i N_j d\Omega \qquad [22]$$

$$k_{ij} = \int_\Omega \nabla N_j . (k \nabla N_i) d\Omega \qquad [23]$$

$$f_i = \int_\Omega f \, N_i d\Omega \qquad [24]$$

N_i = basis or shape functions

c_{ij} = parameters of capacitance matrix

k_{ij} = parameters of conductance matrix

Accurate evaluation of these integrals in equation is difficult in the phase change region because for problems involving a change of phase within a narrow band of temperatures, the curves of thermal properties versus temperature is not smooth. Different numerical approximation is used to appropriately approximate the thermal properties at the phase change boundary. It has been pointed out that the graph of enthalpy versus temperature is sufficiently smooth even over the phase change interval interpolated for the enthalpy, instead of heat capacity and we can approximate the enthalpy by the same shape functions used to approximate the temperature (Comini et al, 1974; Lewis & Roberts, 1987; Tamma & Namburu, 1990);

$$H = N_i(x_i)H_i(t) \qquad [25]$$

H_i = the enthalpy values at nodes

N_i = usual interpolation function within an element

Various approximations appear in the literature for evaluating the heat capacity as a change of enthalpy at the nodes with respect to temperature;(Lewis & Roberts, 1987)

$$\rho c = \frac{dH}{dT} \qquad [26]$$

In a Galerkin finite-element approximation the conductivity need to be evaluated at the integration point. An approach would be to use a linear interpolation of the nodal conductivity. In case where there is a discontinuity in the thermal conductivity, the integration point values can be evaluated using an averaging scheme (Voller & Swaminathan,1993). All the elements integrals are strongly dependent on the thermophysical properties and consequently temperature, thus repeated evaluation of element integrals for changes in thermophysical properties is accomplished using numerical integration (Burnet,1987).

1.7.3 Time Discretization

The matrix equation [21] contains the undiscretized time derivative of temperature. The next step following the semi-discretization process is the solution (or time discretization) of the ordinary differential equations [21] which define the discretized thermal model.

The discretization of the time derivative is most often achieved with a finite difference technique. Almost all the time stepping methods have actually been used in commercial finite element codes and almost all of them can be classified as linear multistep method. For finite element application, one and two step methods are used almost universally for diffusion problems. The one step methods include three classical finite difference formulas (Bonacina et al, 1973; Comini et al, 1974; Morgan et al, 1978; Voller et al, 1981);

1- the backward difference method, known as the backward Euler rule.
2- the mid-difference method also known as the Crank-Nicolson method or the trapezoidal rule
3- the forward difference method also known as Euler's rule
4- the two-step or three-time-level scheme referred to as the Dupont II scheme
5- the two-step or three-time-level scheme proposed by Lees.

The first three methods are special cases of a more general formula referred to as θ-method. This family of methods can be characterized as follows;

$$C^{n+\theta}(T^{n+1}-T^{n})/\Delta t+K^{n+\theta}(\theta T^{n+1}+(1-\theta)T^{n})=F^{n+\theta},\quad 0<\theta<1 \qquad [27]$$

n= number of the time increment

Δt = length of time increment

C = capacitance matrix

K = conductance matrix

F = thermal loading matrix

T = temperature

The θ-method is unconditionally stable with θ>1/2 for both linear and non-linear conduction. The most favored schemes are;

θ = 1/2	Crank-Nicolson
θ = 2/3	Galerkin scheme
θ = 1	Euler-backward

Of the various time-integration schemes available, it has been observed in the literature (Dalhuijsen, Segal,1986) that the Euler backward is one of the most favorable of the θ-methods for solidification problems in terms of acceptable accuracy, efficiency and easiness of implementation. In this method thermophysical properties are evaluated at time level n+1 and an iterative solution method is necessary.

1.7.4 Elements

A geometry can be represented by a combination of different finite elements. Most of the proposed elements that have been used in the stress analysis of solids are applicable to heat transfer problems. However for transient phase change problems, usually linear elements are used. For these elements the temperature field in each element is approximated by a linear function. For one dimensional linear elements, the general form of this function is, figure 1.4;

$$T(x,t) = \alpha_1(t) + x\alpha_2(t) \qquad [28]$$

α_1, α_2 = coefficients of linear approximation for temperature distribution in an element

where T(x,t) is the temperature distribution in each elements and $\alpha_1(t)$ and $\alpha_2(t)$ are obtained from nodal temperature at each time step. Although various types of elements could be employed for general finite element analysis of the thermal problems, for solidification problems, the use of linear elements is often recommended, since significant

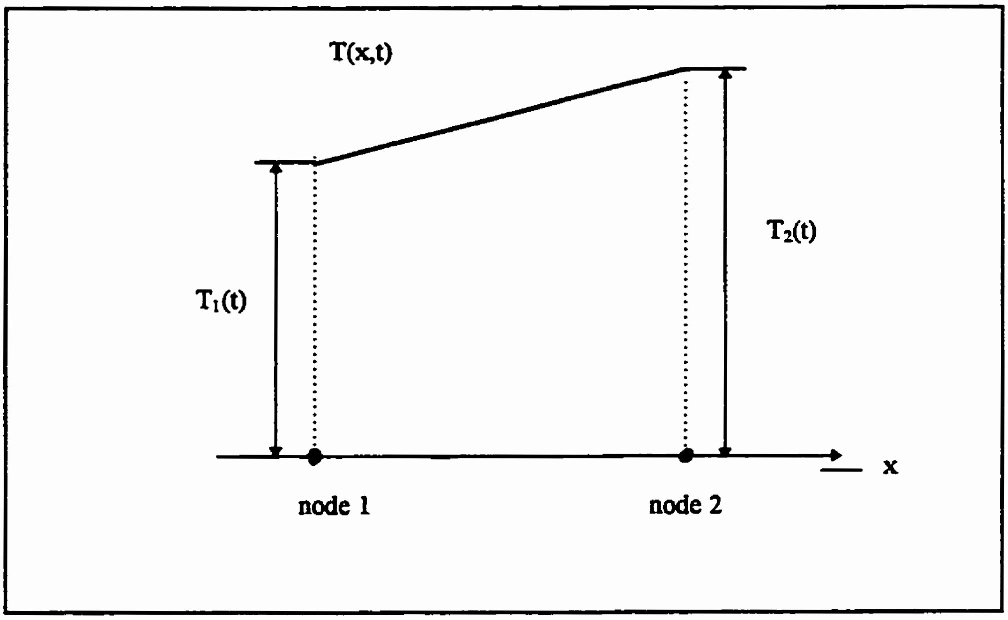

Figure 1.4: Finite element temperature approximation within an one dimensional linear element.

improvements cannot be expected with higher-order elements. This is because there are sharp discontinuities in the associated derivatives of the temperature in the vicinity of the phase front (Dalhuijsen & Segal, 1986 and Tamma &. Namburu, 1990).

1.7.5 Time Step Size

A suitable combination of time step and phase change interval will result in a good approximation for the analytical solution. The time step used should be such that the change in temperature during one time step in a region undergoing a change of phase, be less than the temperature difference over which the phase change is assumed to occur. If this is not so, a correct heat balance may not be maintained and incorrect solution will result. When using Euler-backward time stepping scheme, although very few iterations are necessary to satisfy the convergence criterion for the latest time steps, in the initial ones more iterations are needed, leading to an average of about 1.8 iterations per time step over 50 time steps. Ralph III & bathe (1982) have already mentioned that a fine space discretization and small time steps are necessary for accurate temperature predictions, whereas the freezing front could be accurately monitored with coarse grids and larger time steps.

The start time t_0 is chosen for each parameter regime to ensure that any heat transfer in the time $t<t_0$, is confine to a region closed to the interface between the two regions and the outer extremities are not affected.

1.9 Melting Range

Dalhuijsen and Segal (1986) have shown that the size of the induced freezing (melting) range has little effect on the temperature and since the freezing front position is obtained from temperature by extrapolating from the solid side, the imposed freezing temperature range hardly affects the accuracy of the predicted front position.

In the cases when phase-change occurs at a specific temperature, using enthalpy method, we should consider a small temperature range for the phase change. Although the size of the freezing range has little effect on the error in the temperatures or freezing front position, a small freezing range is to be preferred since it gives a better representation of the actual Stefan problem. In the case of existence of a melt range for the material, at any time an area of the body will be undergoing melting rather than a point. This area of melting is referred to as the 'mushy' region and is bounded by a solidus and liquidus boundary.

Also there is the possibility of the temperature at a node 'skipping' the phase change temperature interval in a single time step of the numerical fixed-domain computations if the interval is too small, the grid not dense enough or the time step too large. Thus severe restrictions are imposed on the execution of calculations. Bonacia & Comini (1973) suggest that the phase change interval must embrace at least 2-3 nodes along the direction normal to the interface.

1.10 Front Position

Goodrich (1977) introduces an accurate method for determining the solid-liquid interface movement when the phase change occurs on a narrow temperature range. He tested his method in one dimendional problems and obtained good results. Voller and Cross (1981) suggest a method for calculating the position front between the nodes at each time step, for a welding problem with steel. They use interpolation on the temperature distribution and calculated the position of solidus boundary at time $t=j\delta t$ from;

$$\text{Solidus} = [S^{*} + (t_s^j - T_{m+\varepsilon})/(t_s^j - T_{s+1}^j)]\delta x \qquad [29]$$

S^{*} = fraction of the element which is solid

T_s = solid temperature

$T_{m+\varepsilon}$= upper limit temperature for the temperature range

j = Number of time increment

δx = element length

Voller and Cross (1983) have mentioned that the solidification front position, when using enthalpy method, follows the predicted temperatures. They recommend a scheme in which linear interpolation is used to find the time at which the solid-liquid interface is at a mesh point and show when enthalpy is defined in a small temperature range, temperature histories will only be predicted when at least two nodal temperatures lie in the phase change range at all time steps.

Dalhuijsen and Segal (1986) show that the method for calculating the freeze front position was examined and the extrapolation of the temperatures from the solid side to give the position corresponding to the melting temperature seemed to be most appropriate. But they also mentioned that, care must be taken, since errors in the nodal temperatures used in the extrapolation may be amplified. They note that interpolation of temperatures across the phase change to found the position where temperature is equal with melting temperature is objectionable. However, they used the method suggested by Voller and Cross (1981) in their calculation and find good approximation to the exact solution available for their problem.

Interpolating or extrapolating to give the position corresponding to

$$T = T_m - \Delta T_m \tag{30}$$

T_m = melting temperature

ΔT_m = half of the melting range

results in poor results when temperature range is relatively large and is confusing since the actual freezing temperature is T_m.

Chapter 2

Phase Transition in Polymers

2.1 Introduction

We can distinguish between two main kinds of melt solidification processes for polymers, static solidification, which is defined as a process where there is no relative motion between adjacent polymer layers, like in compression molding, and flow solidification where the melt solidifies during flow in the filling stage as in injection molding.

Heat transfer in polymers in the solidification (or melting) process is accompanied by change of phase, melt to solid in the case of crystalline polymers and melt to rubber to glass in the case of amorphous polymers. Not only phase transition is different for semi-crystalline and amorphous polymers, but also thermophysical properties of these materials differ for the same polymer and are highly dependent on molecular structure and thermal history of the material.

In the processing of polymers, the temperature gradients are large, since their thermal conductivities are low, the process times are small, then the local thermodynamic equilibrium theories seldom hold. The heat required to melt plastics is large and the rate at which it can be put into the plastics is limited by the thermal conductivity and the thermal stability of the material. In several cases, the high temperature on the outside would cause decomposition and burning before enough heat could penetrate to the melt, the mass of material.

In this chapter we investigate briefly, the phase transition in polymers, their thermophysical properties and their affects on determining the processing parameters.

2.2 Heat Transfer in Polymers

We should be concerned by the excellent thermal insulating properties of plastics in both the solid and fluid states. Thus, not only are the fluids of high viscosity, but the mode of heat transfer during laminar flow is conduction or diffusion. Since plastics have such a poor thermal conductivity, transfer of heat to or from molten plastics in flow and solid plastics in static cases is very difficult. Little heat is transferred by convection because the melt is too viscous. Radiation, although having some effect, accounts for only a very small proportion of the total heat transferred. According to Rosato(1986) heat transfer in the mold is almost entirely by diffusion.

2.3 Phase Transition in Amorphous and Crystalline Polymers

Since phase-change for crystalline polymers is a first order transition in which a primary thermodynamic functions, such as enthalpy shows a sudden jump, the change of energy with temperature, at a phase change such as melting, a discontinuity in the specific heat curve should occur at the melting point temperature. But for amorphous polymers, glass-rubber transition is a phase change of a thermodynamic second-order transition. In the case of second-order transition a plot of a primary quantity shows an abrupt change in slope, while a plot of a secondary quantity, like specific heat, shows a sudden jump. Generally speaking, crystalline and amorphous polymers are different from the heat transfer point of view by the fact that crystalline polymers generate latent heat upon solidification while amorphous polymers do not. The melting temperature can not be defined for a noncrystalline or amorphous polymer, it simply does not solidify. One characteristic temperature that is important in amorphous polymers and to a lesser extent in crystalline polymers is the glass-transition temperature, T_g. The glass transition temperature is best defined as the temperature below which a polymer changes from a rubbery substance to a glassy substance. The exact position of T_g is affected by the rate of cooling, the slower the cooling process the lower will be the value of T_g. Yet for practical purposes one can say that every polymer is characterized by its own T_g (Van Krevelen, 1990).

Many plastics have crystalline structures in their solid form. As a result, if these solid materials are heated slowly to liquid state, a distinct melting temperature associated with a given material can be identified within 1°C or so. Therefore for semi-crystalline polymers it is possible to identify a melting temperature T_m. Above this melting temperature the polymer may be liquid viscoelastic or rubbery according to its molecular weight. Below it, at least in high molecular mass range, it will tend to be leathery and tough down to glass transition temperature. The crystalline melting point T_m is the highest temperature at which polymer-crystallites can exist (Van Krevelen, 1990). For crystalline materials, the glass-transition temperature is important too, because crystallization can occur only between T_g and T_m.

The problem of unsteady-state heat transfer associated with the melting of crystalline plastics and with the cooling of such melts after they have been filled into the molds, is complex. As mentioned before, when these plastics change from the liquid to the solid state or vice versa, a latent heat of fusion must be added during melting or taken away during cooling. This process occurs at a specific temperature, and it causes a delay in temperature change. Partially crystalline polymers exhibit a freezing range. Instead of a complete delay of temperature when the upper limit of the melting range is reached, only a partial delay proportional to the crystallization fraction is applied. Thus one part of the heat contributes to lowering the temperature of the amorphous portion, while the other part is utilized in freezing the crystalline portion. The partial delay in the temperature reduction is terminated when the lower limit of the freezing range is obtained. In the phase change analysis of amorphous polymers, however, melting temperature can be replaced by glass transition temperature (Kamal et al, 1970 & 1971). Generally the heat required to melt semi-crystalline plastics at a given temperature exceeds that of amorphous plastics at the same temperature (Throne,1979).

2.4 Thermal Properties of Polymers

Most polymer samples are partly crystalline. The thermodynamic quantities have values somewhere between the purely crystalline and purely amorphous regions. Polymer thermal properties are highly dependent on density, molecular weight, orientation and other factors.

The discussions in this section are confined to three polymer properties: thermal conductivity, thermal diffusivity and specific heat capacity.

2.4.1 Thermal Conductivity

The thermal conductivity of polymers are low, on the order of 0.1-0.5 W/ m.K. Among polymeric substances, crystalline polymers tend to have higher thermal conductivity than amorphous polymers

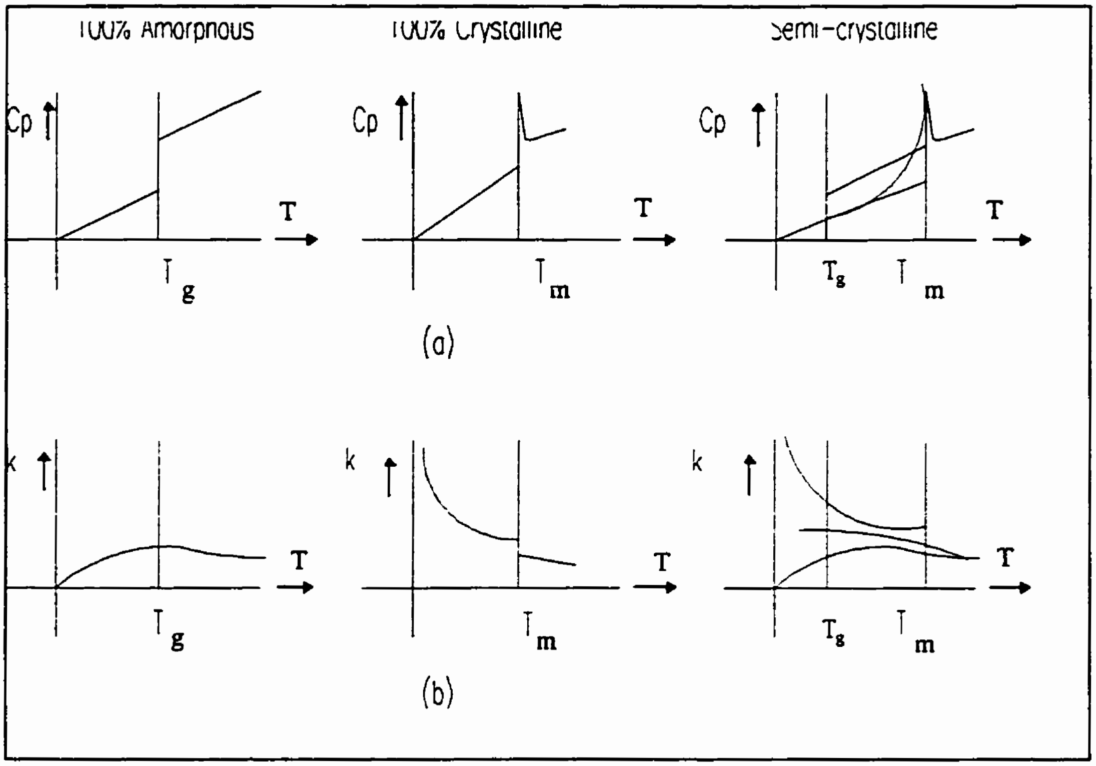

Figure 2.1: Behavior of some polymer properties at transition temperatures. (a) Specific heat, (b) Thermal conductivity

For polymeric systems the change of thermal conductivity with temperature is generally small or negligible. By increasing the temperature the amorphous polymers thermal conductivity increases slowly in the glassy region. It is constant or slowly decreasing in the rubbery region, and passes through a rather flat maximum at glass transition temperature. Finally, it shows a graduate decline in the liquid state. In crystalline polymers thermal conductivity decreases steadily as the melting point is approached. Otherwise, it behaves in a manner analogous to amorphous polymers, figure 2.1b.

Analysis of the available literature data for identical or nearly identical materials indicates large differences in reported thermal conductivity and the temperature dependencies exhibit different functional relationships, particularly at higher temperatures (Hall et al, 1987).

2.4.2 Specific Heat Capacity

Although polymers have much lower densities than metals, they have relatively large specific values, typically in the order of 750-2500 J/Kg.K. The temperature dependence of specific heat capacity is of importance. In general a small discontinuities is observed at the glass transition temperature T_g, followed by a relatively large peak at melting point, T_m, due to the latent heat of fusion of the crystalline domain. All polymers display similar temperature dependencies, although the curve shifts horizontally along the temperature axis, depending on where T_g and T_m occur, and vertically along the heat capacity axis, depending in the absolute values of heat capacity itself, figure 2.1a. A crystalline polymer follows the curve for the solid state to the melting point. At T_m the value of C_p increases to that of the liquid polymer. The heat capacity of an amorphous polymer follows the same curve for the solid up to the glass transition temperature, where the value increases to that of the liquid (rubbery material). In general a polymer sample is neither completely crystalline nor completely amorphous. Therefore in temperature region between T_g and T_m the heat capacity is between the curves for solid and liquid.

Molecular weight has a small but appreciable effect on specific heat capacity. The thermal history of a polymer may influence the specific heat capacity. Similarly, cooling rates may effect the degree of crystallinity as well as the amount of recrystallization that takes place on reheating above the glass transition temperature.

Specific heat capacity may be defined at constant volume or at constant pressure.

2.4.3 Thermal Diffusivity

Like thermal conductivity, thermal diffusivity of polymers is low. Therefore, most processing and fabricating techniques involve unsteady state heat transfer where temperatures are a function of both position and time. Thermal diffusivity of polymers are is the orders of $0.1\text{-}0.3\times10^{-6}$ m^2/s

In amorphous polymers, thermal diffusivity decrease slowly in the glassy region, break slightly at the glass-transition temperature and remain essentially constant in the rubbery region, and decrease slowly in the melt flow region. In crystalline polymers thermal diffusivity has similar characteristics but displays a relatively deep minimum at the melting point, figure 2.2.

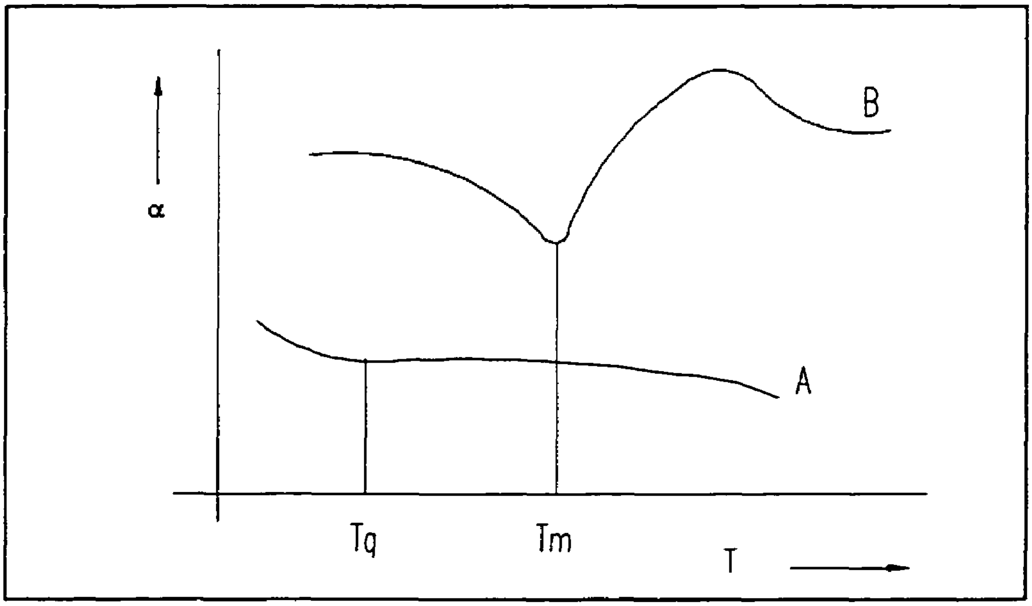

Figure 2.2: Thermal diffusivity vs. temperature.Curve A, a typical amorphous polymer, Curve B, a typical partially crystalline polymer

2.4.4 Latent Heat of Crystallization and Fusion

The heat added to the polymer causes a change in the internal energy U, and the enthalpy of the substance.

The latent heat of fusion (crystallization) or enthalpy difference is defined by;

$$H_l(T_m)-H_c(T_m)=\Delta H_m(T_m) \qquad [27]$$

$H_l(T)$ = Enthalpy of melt as a function of temperature

$H_c(T)$ = Enthalpy of solid as a function of temperature

ΔH_m = Enthalpy of fusion

T_m = Melting temperature

Reliable experimental values for ΔH_m are available for a limited number of polymers only. In a direct determination the degree of crystallinity of the sample should be taken into account. In this connection, a large scatter in published values for enthalpy of fusion is observed, as a general rule the highest value of ΔH_m mentioned for a given polymer is the most probable one (Van Krevelen, 1990).

The enthalpy curves for crystalline and amorphous polymer run parallel up to the glass transition temperature. The distance between these curves is the enthalpy of the amorphous polymer. From the glass transition temperature the curve for the amorphous polymer gradually approaches the curve for the melt, while the curve for crystalline polymer shows a discontinuity at the melting point. The distance between the curves for crystal and liquid at the melting point is the latent heat of fusion.Figure 2.3.

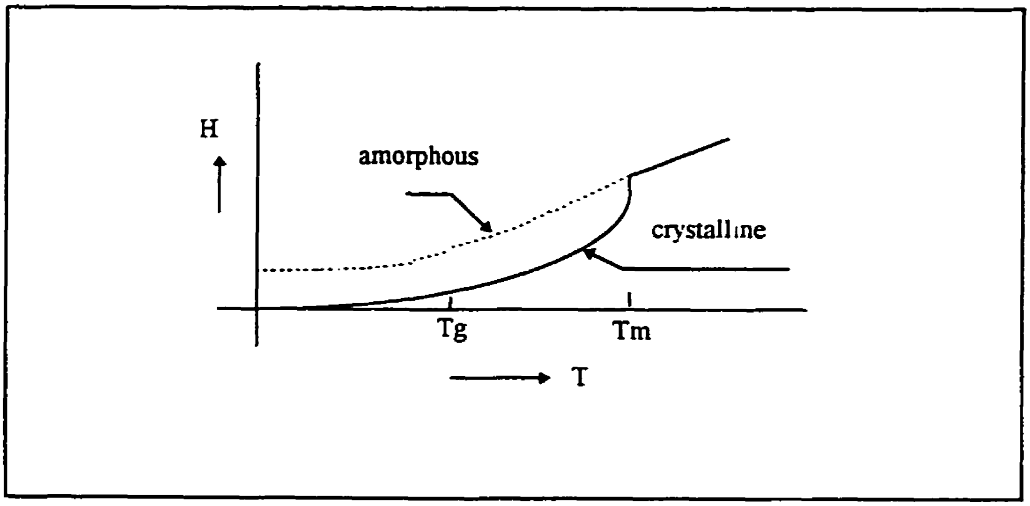

Figure 2.3: Enthalpy variation with temperature.

Chapter 3

Model

3.1 Problem Definition

Here the process of injection of a molten thermoplastic over a solid thermoplastic insert is studied, figure 3.1. The process is similar in concept to welding or dip coating of polymers. In order to obtain a strong and uniform joint between the molded part and its insert we follow the process of phase change at the interface between melt and solid. The resulting heat transfer process may progress in many different ways dictated by the parameters involved in the system. In the way to reach steady state heat transfer condition, melt-solid interface moves, from its initial position, to a certain depth before the two parts begin to solidify together and join as a single piece.

In order to widen the range of physical and mechanical properties of the piece, we have to consider the effects of different parameters and molding conditions, on the evolution of the solid-melt interface.

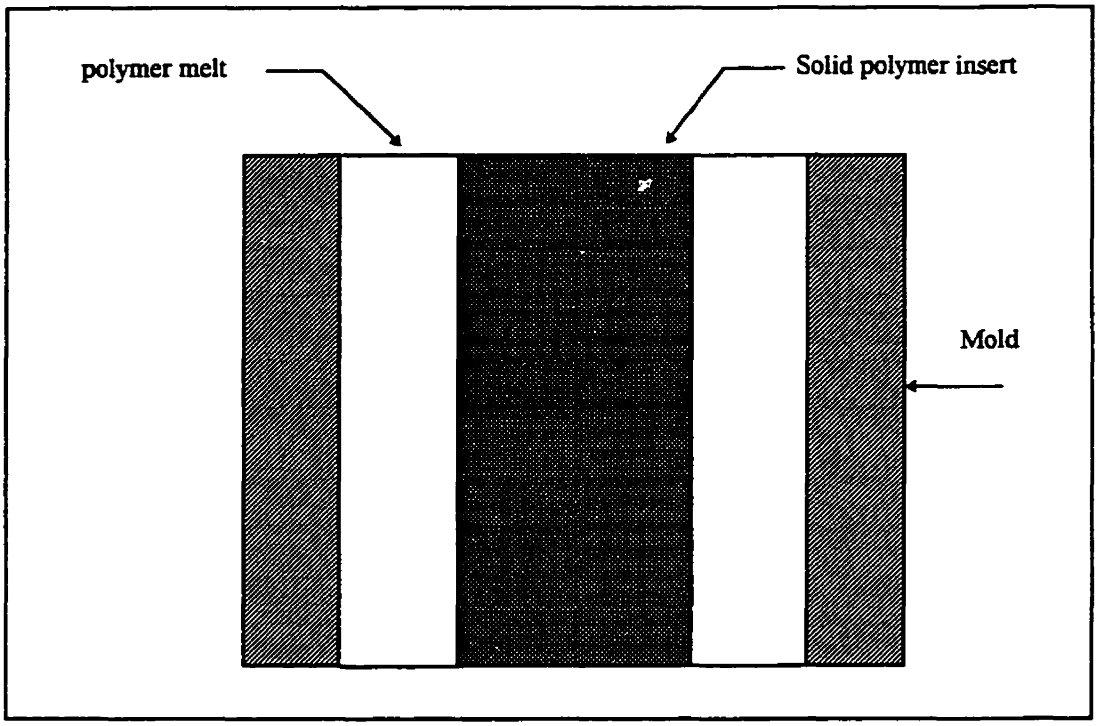

Figure 3.1: Schematic of the part in the mold

3.2 Mechanism of Heat Transfer

Figure 3.2 shows the mechanism of heat transfer. Heat is conducted from the molten region to the solid and also there is a heat flow between the mold wall and polymer melt by conduction. At the solid-melt interface, the process of heat transfer is by conduction where all the heat is provided by contact on the exposed surfaces and the rate of melting is only determined by conduction.

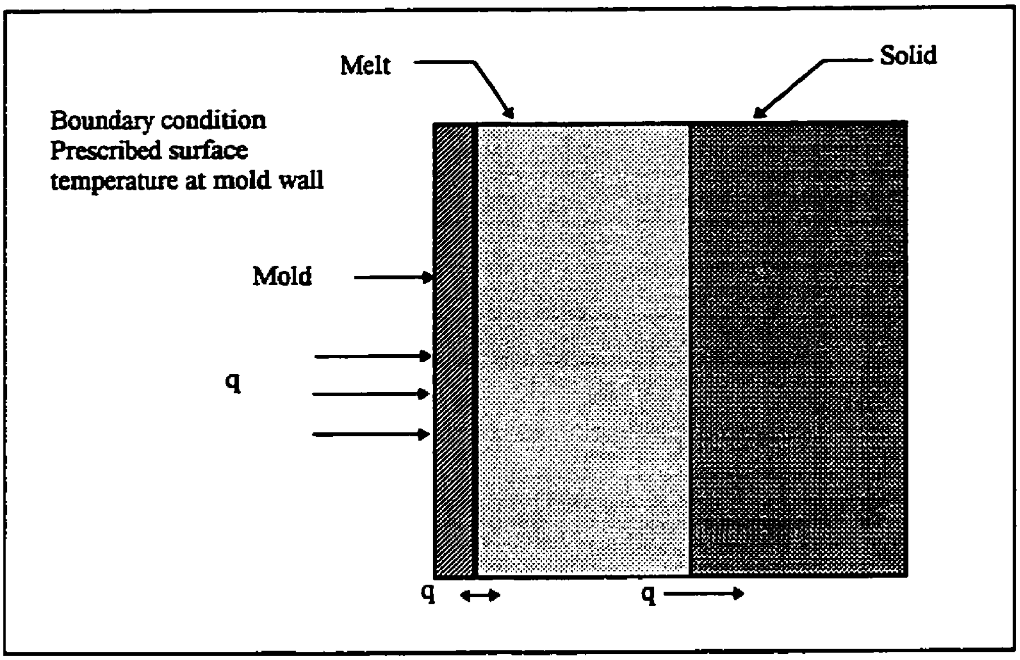

Figure 3.2: Heat transfer mechanism in the mold

3.3 Introducing a Mathematical Model

This model is developed for the situation where the mold has been totally filled. In that case, the changes in the polymer temperature, may be determined by solving the unsteady state heat conduction equations with change of phase since the polymer is stationary. Since the polymer melt is extremely viscous, In the following treatment, it is assumed that the natural convection is negligible.

3.3.1 Hypothesis

To formulate this problem it is assumed that;

1- The effect of second and third coordinate system is so small that it can be neglected

2- Thermophysical properties are taken to be invariant to temperature (for PET)

3- Mass densities of the melt and its solid are assumed to be the same.

4- The phase change of pure substance with a precise fusion and freezing temperature is modeled.

5- The temperature at mold wall will remain constant during the process

6- No chemical reactions or massive absorption of heat take place during temperature change.

3.3.2 Geometry and Coordinate System

We assume that the coordinate system for this problem is arranged as in figure 3.3. A solid confined to a semi-infinite region, $A<x<B$. Initially the solid is at uniform temperature, T_{is}, which is lower than the phase change temperature T_m. The melt occupies the space $0<x<A$. The solid and the melt will remain in contact for $t>0$.

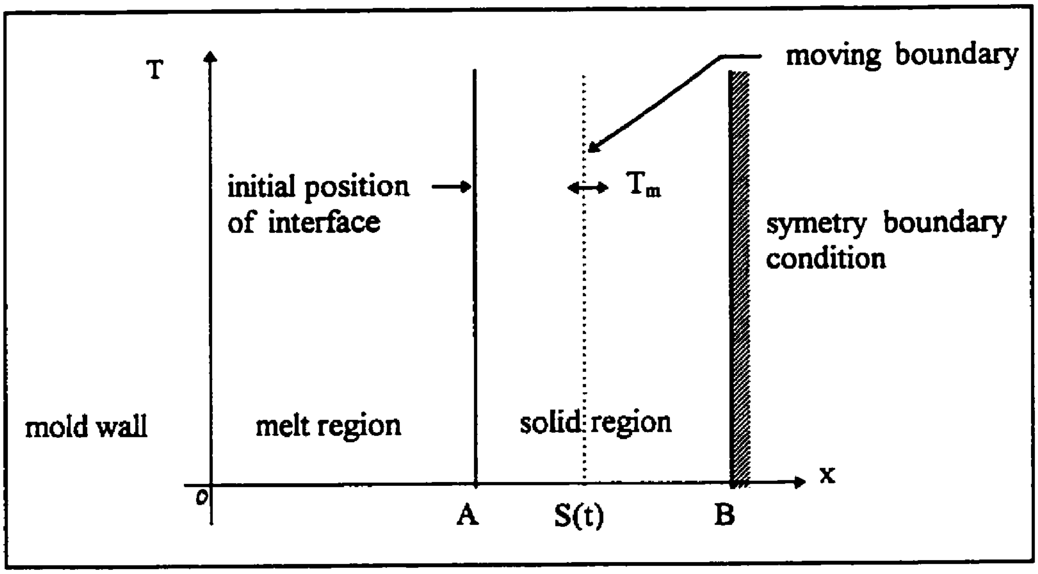

Figure 3.3. Geometry and coordinate system

The boundary surface of the melt at x=0, the mold wall, is at constant temperature T_w. The boundary surface at x=B, is in the condition of symmetry.

3.3.3 Mathematical Formulation

(a) Governing Differential Equations

Now we can simplify the general energy equation by considering these assumptions. The temperatures $T_s(x,t)$ and $T_l(x,t)$ for the solid phase and liquid phase respectively are governed by the standard fusion equation given by;

$$
\begin{aligned}
k_l(T)\frac{\partial T_l(x,t)}{\partial x} &= \rho c_{pl}(T)\frac{\partial T_l(x,t)}{\partial t} \qquad && 0 < x < S(t) \\
k_s(T)\frac{\partial T_s(x,t)}{\partial x} &= \rho c_{ps}(T)\frac{\partial T_s(x,t)}{\partial t} \qquad && S(t) < x < B
\end{aligned}
\qquad [31]
$$

k_l = melt thermal conductivity

k_s = solid thermal conductivity

T_l = melt temperature

T_s = solid temperature

c_{pl} = melt specific heat at constant pressure

c_{ps} = solid specific heat at constant pressure

$S(t)$ = interface positions as a function of time

ρ = density

(b) Initial and Boundary Conditions

The equation is a second order differential equation. For each phase we need two boundary conditions and one initial condition:

- Boundary conditions:

$$T_l(x,t) = T_s(x,t) = T_m \qquad x = S(t),\ \ t > 0 \qquad [32]$$

$$T_l(x,t) = T_w \qquad x = 0, \quad t > 0 \qquad [33]$$

$$\frac{\partial T_s(x,t)}{\partial x} = 0 \qquad x = B, \quad t > 0 \qquad [34]$$

- Initial conditions:

$$T_l(x,t) = T_{il} \qquad 0 < x < A, \quad t = 0 \qquad [35]$$

$$T_s(x,t) = T_{is} \qquad A < x < B, \quad t = 0 \qquad [36]$$

T_{il} = melt initial temperature

T_{is} = solid initial temperature

T_w = wall temperature

S(t) is the location of the solid-liquid interface which is not known a priori, hence must be determined as a part of the solution.

This problem involves the unknowns, $T_s(x,t)$, $T_l(x,t)$ and S(t). The third equation is determined by considering an interface energy balance at x=S(t);

$$k_s(T)\frac{\partial T_s(x,t)}{\partial x} - k_l(T)\frac{\partial T_l(x,t)}{\partial x} = \rho L\frac{dS(t)}{dt} \qquad x = S(t), \quad t > 0 \qquad [37]$$

L = latent heat of fusion

3.4 ABAQUS

3.4.1 Finite Element Method

As explained before because of the complexity of the equations there is no exact solution for the problem. Approximate solutions that are available covers only very simple cases with simple boundary conditions, we should choose a numerical approach to solve the equations. We have used ABAQUS to solve this problem with finite element method. The capability of ABAQUS for uncoupled heat transfer analysis is intended to model solid body heat conduction with general, temperature dependent conductivity, internal energy including latent heat effects and quite general convection and radiation boundary conditions. In programming with this software, it is assumed that the thermal problems are presented in the form;

$$U = U(T) \qquad [38]$$

U = Internal energy of material

T = Temperature

The change of internal energy of the material with respect to temperature is written in terms of specific heat (enthalpy method);

$$C(T) = \frac{dU}{dT} \qquad [39]$$

For latent heat effects at phase change, this relation is given separately in terms of solidus and liquidus temperatures (the lower and upper temperature bounds of the phase change) and the total internal energy associated with the phase change, called the latent heat. When latent heat is given, it is assumed to be in addition to the specific heat effect, as explained in detail in section 1.6.

To define the latent heat effects for the materials with specific melting temperature, a small temperature range should be considered. However, to avoid large deviation of the solution from the real physical situation we should consider this temperature range as small as possible around the real melting point of the material. The Fourier law of heat conduction can be solved, considering the change of thermophysical properties of the material. To apply finite element formulation, the standard Galerkin approach is used.

ABAQUS uses the backward difference algorithm for time discretization in finite element method. This operator is chosen for a number of reasons. First of all, it is from the family of one step operators which has the simplicity in implementation and well understood behavior among the members of this family, backward difference method, is unconditionally stable. Being unconditionally stable is important because it prevents early time oscillations. ABAQUS uses an automatic(self adaptive), time stepping algorithm to choose Δt(time increment). This is based on a user supplied tolerance on the maximum temperature change allowed in a time increment, and increment is adjusted according to this parameter, as well as the convergence rate in non-linear cases.

3.4.2 Type of element

All of the heat transfer elements allow for heat storage (specific heat and latent heat effects) and heat conduction. These elements are either first-order (linear), or second order (quadratic) interpolation in 1,2 or 3 dimensions. They are fully isoparametic (coordinate interpolation is the same as temperature interpolation). The first order heat transfer elements(2-nodes link, 4-nodes quadrilaterals and 8-nodes brick) use 2x2 rule for numerical integration with the integration stations located at the corners of the element or nodes. Second order elements are to be preferred for problems when the solution will be smooth (without latent heat effects) whereas the first order elements should be used in non-smooth cases (with latent heat).

Latent heat effects involve moving boundary conditions(the melting or freezing front), across which the spatial gradient of temperature, $\partial T/\partial x$, is discontinuous. Simple finite elements, such as the linear and quadratic elements used in ABAQUS, do not allow gradient discontinuities within elements, although they do allow such discontinuities between elements, in the direction normal to their sides. Since the actual problem involves discontinuity surfaces moving generally through the mesh. The best we can do with a fixed grid of simple elements is to use a fine mesh of lowest order elements, thus providing a high number of gradient discontinuity surfaces.

The lowest order one dimensional element for heat conduction in ABAQUS is element type DC1D4 which is a two node linear element and therefore we choose this element.

3.5 Finite Element Model

3-5-1- Mesh

This is a one dimensional heat transfer problem, and since the geometry of the problem is simple, we choose a simple mesh of one dimensional linear element to model the one dimensional space.

The space occupied by the polymers in the mold is divided into two distinct regions, melt and solid. This space is descriticized by a 100, one dimensional linear elements. Since three different thickness ratio of solid/melt has been tried, for each case

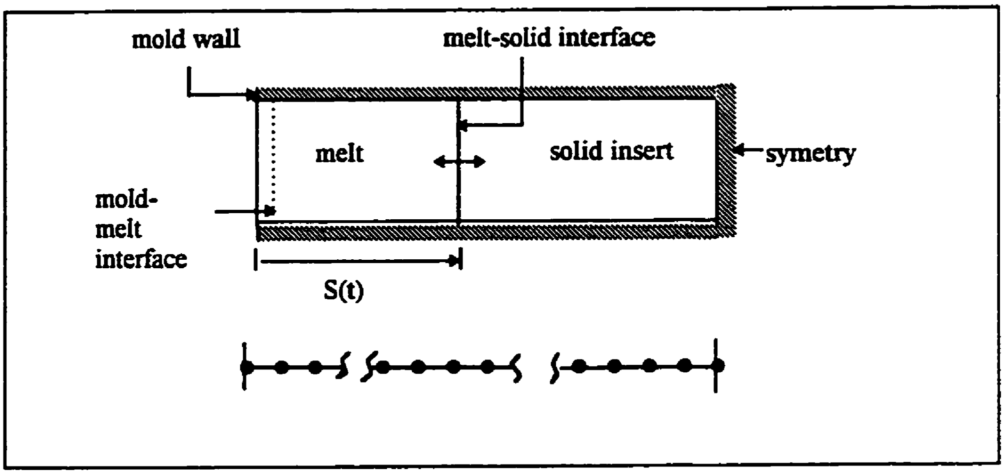

Figure 3.4: One dimensional finite element mesh and geometry

elements are distributed proportional to the thickness ratio. The nodes were generated to coincide with the initial position of the phase change interface. The nodes were set at a predetermined equal spacing. The one dimensional geometry is presented in figure 3.4. Although higher mesh densities and smaller time steps improve the accuracy of the solution, further refinement beyond the values assumed here failed to improve the result significantly. Also coarsing either the spatial to temporal discretization may cause deteriorating and unpredictable results.

3.5.2 Time Step

Due to the sensitivity of these equations, it is necessary to choose the size of the time increment Δt with some care. The start time t_0 is chosen to ensure that any heat transfer in the time $t<t_0$ is confined to a region close to the interface between the two regions and the outer extremities are not affected. Automatic (self adapting) time step, with initial choice of $\Delta t=0.001$ is chosen for time discretization. The program automatically increases this increment as we march forward. A maximum temperature change of 4° is allowed per time step, to allow the time step to increase to large values at later times, as the solution smoothes out. This will considerably reduce the computer time.

3.5.3 Melting Temperature Range

In the case of existing latent heat of fusion for the material. The melting temperature range is given as 1.5° around the melting point (Delaunay, 1995).

3.6 Material

Polystyrene (PS) and polyethylene terephtalate (PET) are chosen to represent amorphous and semi-crystalline polymers. The properties of polystyrene have been extracted from the data given by Van Krevelen in 1990. The change of thermal properties like thermal conductivity and heat capacity with temperature is calculated according to the formulation in this reference, as it is explained in appendix I. These properties are shown in figures 3.5 and 3.6. For this case the change of thermophysical properties with temperature is accounted for in the calculation, although the change of these properties with temperature is small and usually can be neglected.

Table 3.1: Thermophysical properties of polystyrene at room temperature.

Polystyrene	T_g °C	K J/s.m.K	C_p^s(298 k) J/Kg.K	C_p^l(298 k) J/Kg.K
	100	0.1	1220	1720

The properties of polyethylene terephtalate are extracted from Erhun and Advani's work published in 1991. They studied the simple form of this problem and considered the more general form of solution without the change of thermophysical properties with temperature. Kenig and Kamal in 1970, try to take into account these changes in their model of cooling phase of polyethylene in injection molding, They review their work in 1971, in this later publication they generalize their model by eliminating these changes and still they obtain acceptable results.

In the phase change of semicrystalline polymers, because of latent heat of fusion and complexity of the calculation procedure, we cannot expect large improvements in the results by considering the thermophysical properties change. Also because of limited data available, we decided not to consider these changes and take directly the data from Erhun and Advani's work. These data are shown in table 3.2 for PET.

Table 3.2. Material properties of PET.

	T_m °C	K W/cm.K	C_P J/g.K	ρ g/cm^3	L J/g	α cm^2/s
PET	**250**	**0.0014**	**1.4**	**1.385**	**60**	**0.00063**

3.7 Processing Parameters

No doubt, there are different processing parameters and operating conditions, that control the advance of melt interface in the solid (or the advance of solid in the melt) until a specific point. According to Gutfinger & Chen (1969), Bell & Wedgwood (1993), and also Zhang et al (1993) this limiting point is determined by system temperature parameters like solid body temperature, melt temperature and of course the boundary condition, the wall temperature.

A crucial component in simulating solidification (or melting) in the mold is the handling of heat transfer at the interface between the mold and the material, The solution of the equations depends on the selection of boundary conditions. For polystyrene, the problem is studied for three different temperature sets;

I $T_g<T_w<T_l$

II $T_s<T_w<T_g$

III $T_w < T_s < T_g$

These temperatures are shown in table 3.3. The mold temperature differs for each case while keeping the other temperature parameters constant For Polyethylenete tetraphtalate, not only the effect of mold temperature but also the affect of changing the insert temperature is studied. The temperature system for PET is shown in table 3.4.

Table 3.3. Temperature system for polystyrene.

	T_w (°C)	T_{is} (°C)	T_{il} (°C)	T_g (°C)
Case I	110	40	200	100
Case II	80	40	200	100
Case III	30	40	200	100

Table 3.4. Temperature systems for PET

	T_w (°C)	T_{is} (°C)	T_{il} (°C)	T_m (°C)
Case I	100	30	300	250
Case II	120	30	300	250
Case III	120	90	300	250

To generalize the problem, in the case of polystyrene, the differential equations are normalized. Dimensionless parameters are described as follows;

$$T^* = \frac{T - T_w}{T_{il} - T_w}$$
$$t^* = \frac{\alpha t}{l^2}$$
$$x^* = \frac{x}{l}$$
$$c^* = \frac{c}{c_l} \qquad [40]$$
$$k^* = \frac{k}{k_l}$$
$$\rho^* = \frac{\rho}{\rho_l} = 1$$

T_w = Mold temperature

t = Time

α = Thermal diffusivity

l = Total length of solid and melt regions

k_l = thermal conductivity of melt

c_l = specific heat of melt

ρ = Density

and the heat transfer differential equation becomes;

$$\frac{\partial}{\partial x^*}(k^* \frac{\partial T^*}{\partial x^*}) = c_p \frac{\partial T^*}{\partial t^*} \qquad [41]$$

Dimensionless time is the Fourier number. (Fo). It contains the thermal diffusivity and half thickness of the slab. Since the Fourier number is proportional to the reciprocal of the square of the slab thickness, if a section of a plastic part is twice as thick as another one, the time required to cool it to the same temperature will be four times longer than that for the thinner section. Therefore we can say that the limiting point for the advance of melt interface in the solid up to a specific point, is not only determined by melt, insert and mold temperature parameters but can vary by altering the value of X (the ratio of initial melt thickness to initial solid thickness).

For system temperature in case III of table 3.3 and system temperature in case II of table 3.4 we study this affect for three different thickness ratio;

X = 1.0

X = 1/2

X= 2

3.7 Results and Discussion

Figure 3.7-3.18 provide examples of computational results for PET. The freezing mechanism in its early stages is similar to the one obtained for semi-infinite region by Stefan . The reason for this similarity is the low thermal conductivity of the polymer melt resulting in a shallow penetration depth of heat transfer. A comparison between numerical analysis and Stefan's (or Neumann's) theoretical solution for solidification of semi-infinite plate (Appendix II) is shown in figure 3.7. The agreement is good specially for short times, after 10 seconds the deviation is approximately 2% which is expected to increase at longer times because of the difference between the nature of two problems.

Figure 3.8 and figure 3.9 show the temperature distribution for PET and for case I and case II of table 3.4. By increasing the wall temperature or on the other hand, decreasing the temperature difference between the mold and the melt, we can see that the temperature drop becomes slower. Figure 3.10 represents the position of melt-solid interface for PET. For equal initial thickness of melt and solid and temperature system of case I in table 3.4, the melt solidifies and the solid penetrates in melt. The rate of progress of this interface in melt is larger at short times and decays as we approach steady state conditions. As it can be seen in figure 3.11 and 3.12 for the second and third temperature systems of table 3.4, the initial motion of the boundary remains the same as one of freezing of melt, so there is no melting of solid insert. Figures 3.13 and 3.14

shows the temperature distribution for two different thickness melt-solid thickness ratio. By decreasing the quantity of melt simply the quantity of heat that should be removed is lower so the temperature drop is faster in the case of lower thickness ratio. Figures 3.15 and 3.16 show the interface position for two different initial thickness ratio of melt and solid. Still we observe the same initial movement of melt-solid interface, which agrees with Bell and Wedgewood's (1993) predictions, that by altering the value of thickness ratio whilst holding the other parameters constant, the initial motion of the boundary remains the same, but the steady state solution can be varied to literally any position across the spatial region. It is interesting to compare the position of melt-solid interface for the three different temperature systems of table 3.4. Figure 3.17 shows the position of this interface for two different wall temperatures. Because of poor heat transfer properties in the polymer, increasing the mold temperature by 20 degrees does not affect the interface location, while decreasing the insert temperature by 60° C, in figure 3.18, increases the rate of interface movement, which is due to increase in heat transfer rate at melt-solid interface.

It should be mentioned here that it has been shown (Kamal and Kenig, 1970) that the approximate solution depends on establishing a good match between the estimated average properties and the space and time increments employed in the numerical solution. Under optimum stability conditions using approximate thermophysical properties yields temperature profile within 3° C from exact solution but for shorter cooling times, the match is poor and depends on the degree of agreement between the average properties employed in the approximate solution and actual polymer properties at the time under consideration. Also according to this publication, for the time longer than 5 seconds a gap is created at the mold wall, because of polymer contraction, which practically will change this boundary condition. So it should be considered that the value of the initial thickness ratio of melt and solid for short times (less than 5 seconds) is dependent on the properties of material and their changes with temperature.

To investigate the process for polystyrene, the change of thermophysical properties with temperature is accounted for. To make the comparison of the result easier the equations are normalized. Figure 3.19, 3.20 and 3.21 show temperature distribution for three different temperature system of table 3.3 for Polystyrene. For the first temperature system, case I, the temperature in the system moves towards the steady state condition which is the constant temperature equal to T_w (zero dimensionless temperature), figure 3.19. We can see the same revolution of temperature for the case II in figure 3.20, however, in case III, figure 3.21, where $T_w<T_s<T_m$ both the melt and solid temperatures decrease toward the steady state condition which is again the condition of constant temperature all over the system. Figure 3.22 represents the position of melt-solid interface for polystyrene, while considering the temperature system of case I in table 3.3. The wall temperature in this case is higher than the glass transition temperature of the polymer. Therefore we have only one phase change interface. Steady state solution is a condition of constant temperature , all over the system, higher than T_g. Figure 3.23 shows the position of melt-mold and solid-melt interfaces for case II of table 3.3, in

which $T_w<T_g<T_{il}$. As it can be seen in the figure after a short period of time another interface is created near the mold wall, when the two interfaces meet, the temperature is decreased for the whole system, towards the total solid condition. The process begins as the solid melts at low Fourier numbers and melt-solid interface progress in the solid insert until a specific point, $\Delta X^*=0.05$, where this interface begins to move in opposite direction, as the temperature of the system decreases towards the steady state condition, this interface passes through its initial position and towards the mold-melt interface, which indicates the final complete solidification of melt. Figure 3.24 shows the position of interface for further reduction of T_w to 30° C. The mold-melt interface progress more rapidly in melt which is due to larger cooling rate because of larger temperature difference between the melt and the mold. Figure 3.25 compares the position of melt-solid interface at different T_w. As we see for shorter times, reduction of T_w does not affect the position of this interface considerably, but as we proceed in time, big difference can be seen between these curves, the higher the temperature difference between wall and melt, the faster the rate of heat transfer and the faster return of the interface.

In the last two cases we distinguish the advance of melt interface in the solid insert until a specific point. The limiting point is not only determined by system temperature parameters but can vary by altering the value of X. Figure 3.26 shows the progression of phase change front as a function of Fourier number for initial thickness of solid twice the initial thickness of melt. A quick comparison of the melt-solid interface position in this figure with figure 3.24 reveals that the limiting front position is much closer to the initial position of interface, $\Delta X^*=0.025$, and the interface passes through its initial position at lower Fourier numbers. The steady state condition, is a condition of final solidification of the system at temperatures well below T_g. In figure 3.27 we can see that by choosing the initial thickness of melt twice the initial thickness of solid and keeping other parameters constant, the melt-solid interface progresses in solid and cause complete thawing of insert before the solidification layer generated at wall passes through initial position of melt-solid interface. There is no limiting front position for this interface in this case. It can be seen here again that for different thickness ratio the initial motion of boundary remains the same but the steady state solution can be varied and also by decreasing the thickness of the melt, the melt-solid interface returns much faster.

Figures 3.28 & 3.29 show the temperature history for $X^*=0.25$ in melt and point $X^*=0.75$ in solid for three different temperature system of table 3.3. In figure 3.28 it can be seen that the melt temperature decreases steadily as the solid temperature increases, the temperature of these two points converges to the steady state solution which is the state of constant temperature above the glass transition temperature. In figures 3.29 and 3.30 the temperature history of these points is shown for the second and third case of table 3.3. The steady state condition for these cases is the constant temperature all over the system below Tg. Figure 3.31 compares the temperature history for node $X^*=0.25$, in the melt at different wall temperature. Considering that the melt temperature for all three cases, is the same, by decreasing the wall temperature we increase the cooling rate. The affect of this increase in cooling rate, on temperature drop at this point is not large at short times which is due to poor thermal conductivity of polymer melt that slows down the process of heat transfer, for larger Fourier numbers, however, the difference is more pronounced, the lower the wall temperature we recognize the faster cooling of melt and as we approach wall temperature (zero dimensionless temperature), or steady state condition, the distance between the curves decreases. The increase in cooling rate by decreasing the wall temperature is more sensible for higher Fourier numbers which is again due to insulating properties of polymers. For higher Fourier numbers, as we approach steady state condition, the difference between these curves is less pronounced.

As we can see from the results the solution to the heat transfer equations is largely controlled by the boundary conditions used to specify the problem, specially at higher Fourier numbers. However the results of temperature profiles for long times is questionable, the boundary condition between the freezing material and the mold is less well documented. These boundary condition depends on the nature of contact between the freezing material and its container, as well as the heat transfer by the container to external cooling media. It is frequently the case that the rate of heat transfer between the polymer and the mold changes during solidification process. Thermal contact is good early in the process when the material is still liquid, but once solidification begins, thermal contraction of the material reduces the heat transfer rate after an air gap is formed, at the same time the mold heats and expands, contributing further to the gap formation. The relative importance of the gap depends on its size, and on the thermal conductivity of the material and the mold. Although this effect can be investigated in more detail, considering high pressure in the mold in normal injection molding process and short cooling times, the period of interest, the assumption of perfect contact between mold and polymer for our investigation is not far from reality and the results can be considered as a good first approximation for temperature distribution.

The assumption of constant T_W is equivalent to that of a large heat reservoir kept isothermally. In many applications the condition of a constant-temperature reservoir can be approximated because in most cases a plastic melt which is a good insulator is used to coat a metal object, a good conductor. Thus the assumption of constant temperature within the solid is reasonable. It should be emphasized that due to latter assumption larger deviations are expected with objects having a relatively high surface to volume ratio, such as thin inserts. For this cases one would have to replace the constant object temperature with a total heat balance performed on the object. In those cases where these assumptions do not hold the present solution can be viewed as an upper bound on the final freezing (melting) interface position.

Classical theory of Stefan predicts that position of the solidifying front is proportional to the square root of time. He also assumed that the temperature at the crystallization front is constant and equal to the thermodynamic equilibrium melting point temperature this assumption restricts the application of Stefan theory to sufficiently slow processes. Erhun and Advani (1992) claim that energy at the melt-solid interface during crystallization controls the kinetics and subsequently influences the morphology of the transformation. They show that when the crystallization kinetics are taken into account, the heat diffuses at a slower rate, which results in slower front movements. Their results show that the interface temperature is not constant and drops due to the changing crystallization rate which depends on the cooling rate. Their approach coupled the crystallization kinetics through a mathematical model based on the cooling rate of the crystallization domain with the energy equation. The evolving crystallinity and microstructure of the material are modeled by allowing the interface temperature to change with cooling rate. They refer in their work to Kriegl and Eder (1984), who reject the Stefan solution for the modeling of polymer solidification and suggest a numerical model, for the coupling of the cooling rate of the crystallization domain and the energy equation. In another paper, in 1990, however, they try to confirm their numerical model with experiment, but, they were not successful. They explain that the most important feature of this theory is that as soon as the crystallization front is supercooled, there is a chance of nucleation in the bulk of melt in front of the crystallization front. In the above mentioned theory it is clearly assumed that the nucleation can only occur at the crystallization front and not in the bulk, which is mathematically sound but not always realistic, since there are many nuclei in front of the crystallized layer, the growth of this layer is eventually impeded by diffuse crystallization in the bulk. Finally they drawn the conclusion that a crystallization front in the sense of Stefan is surprisingly enough. No doubt that for further studies required to establish a link between material kinetics and heat diffusion, the results obtained using Stefan approach for heat transfer problem of phase transformation can be used as a reliable first approximation in polymer processing.

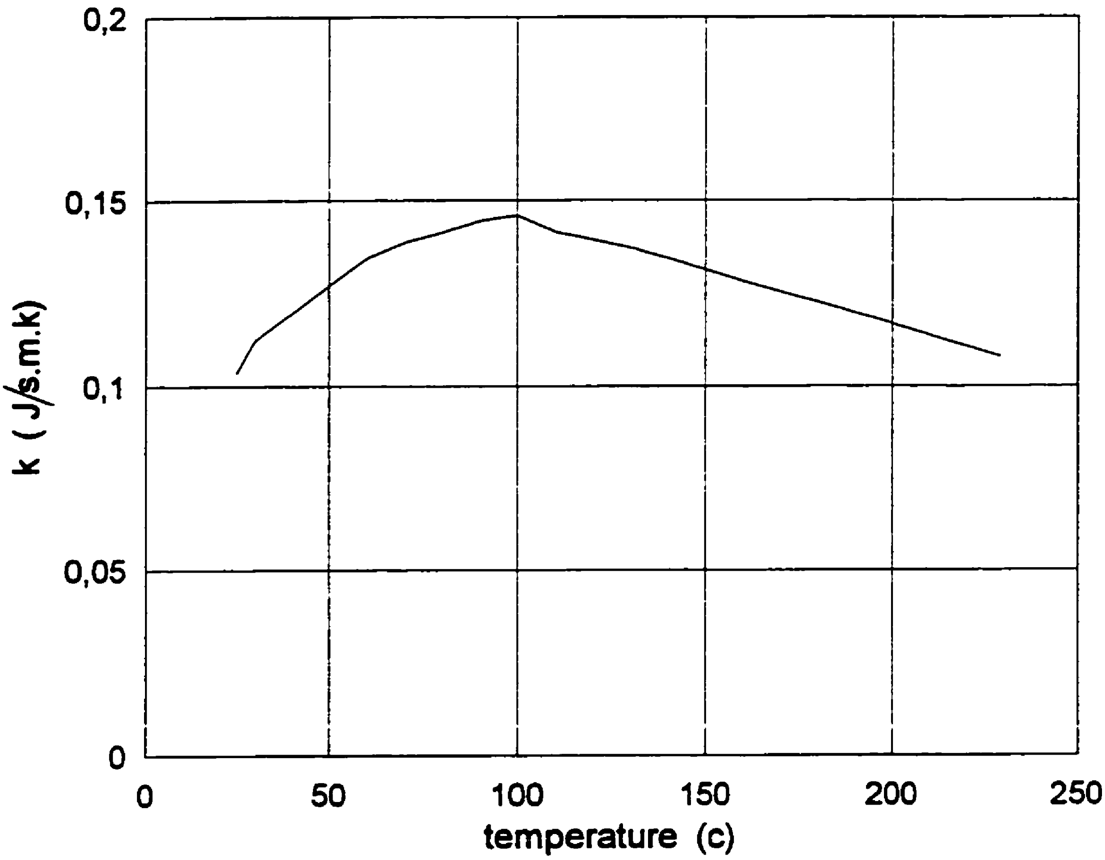

Figure 3.5: Variation of thermal conductivity with temperature for Polystyrene

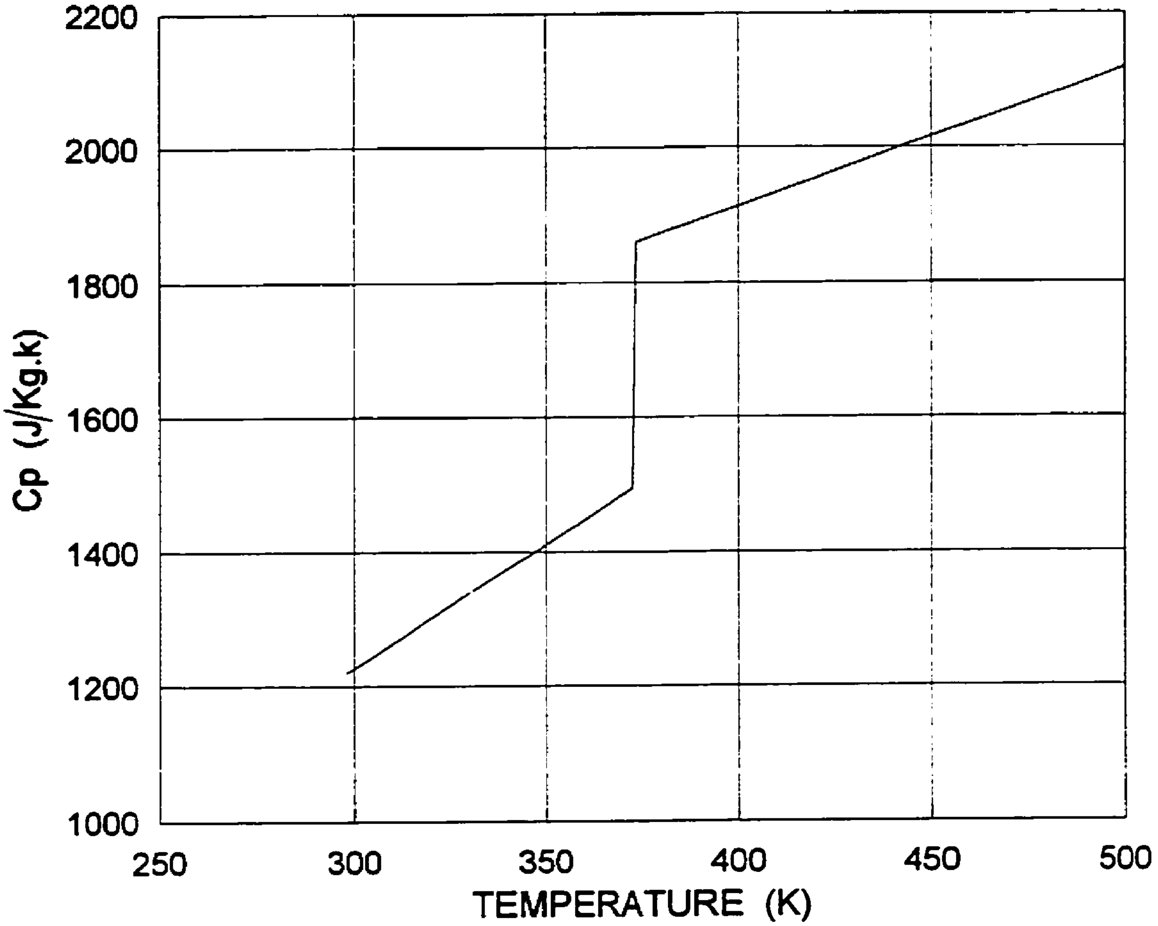

Figure 3.6: Variation of heat capacity with temperature for Polystyrene

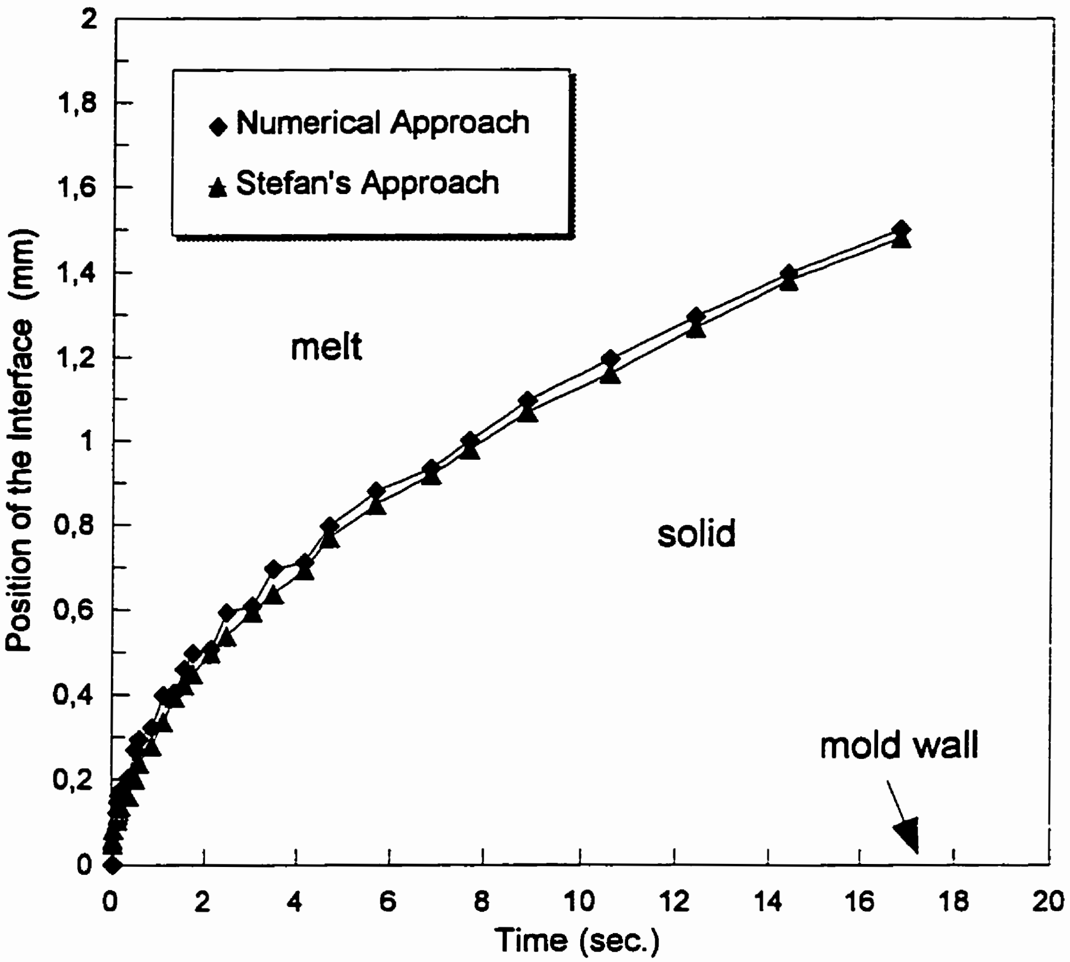

Figure 3.7: Position of phase change interface at mold wall for PET. T_m=250° c, T_i =300° c, T_w=100° c, x_s=x_l

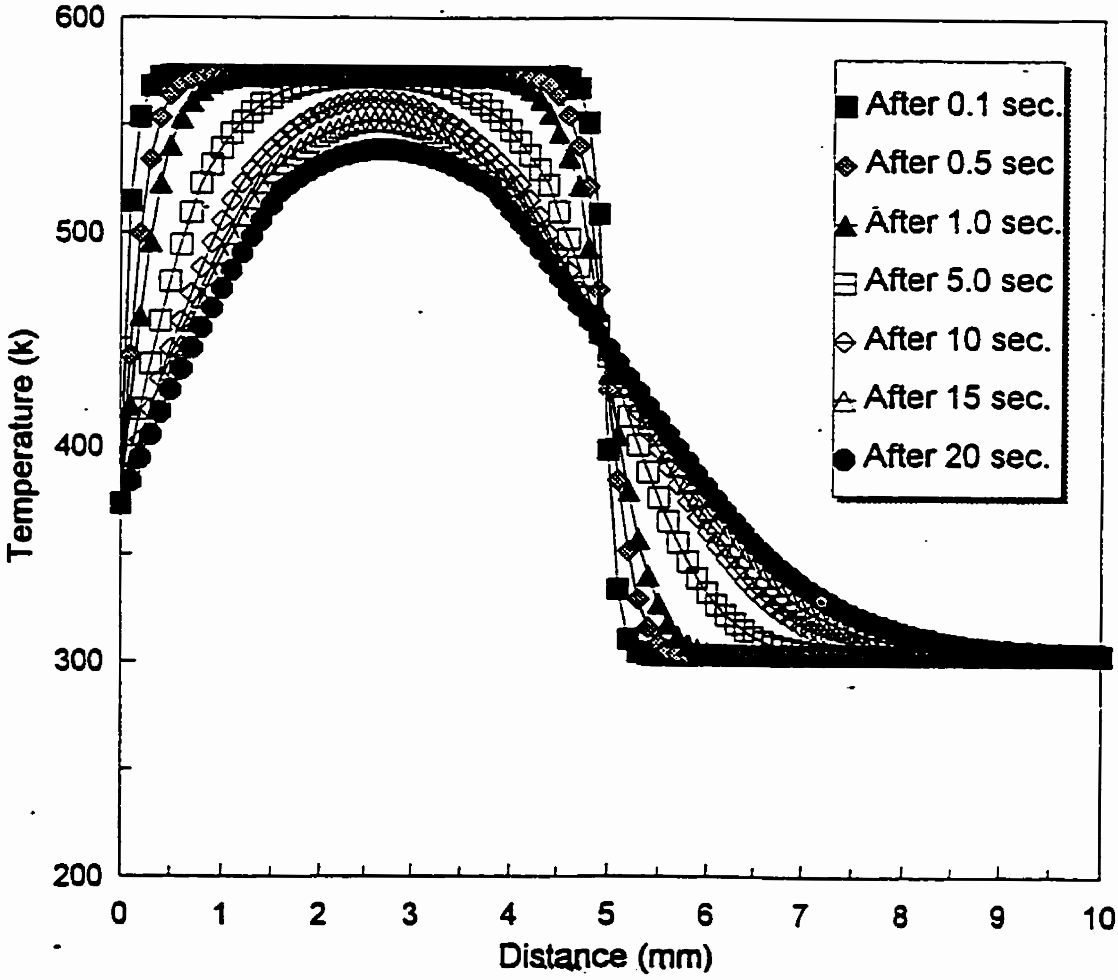

Figure 3.8: Temperature profile at different times in polymer PET, T_w=100°c, x_s=x_l

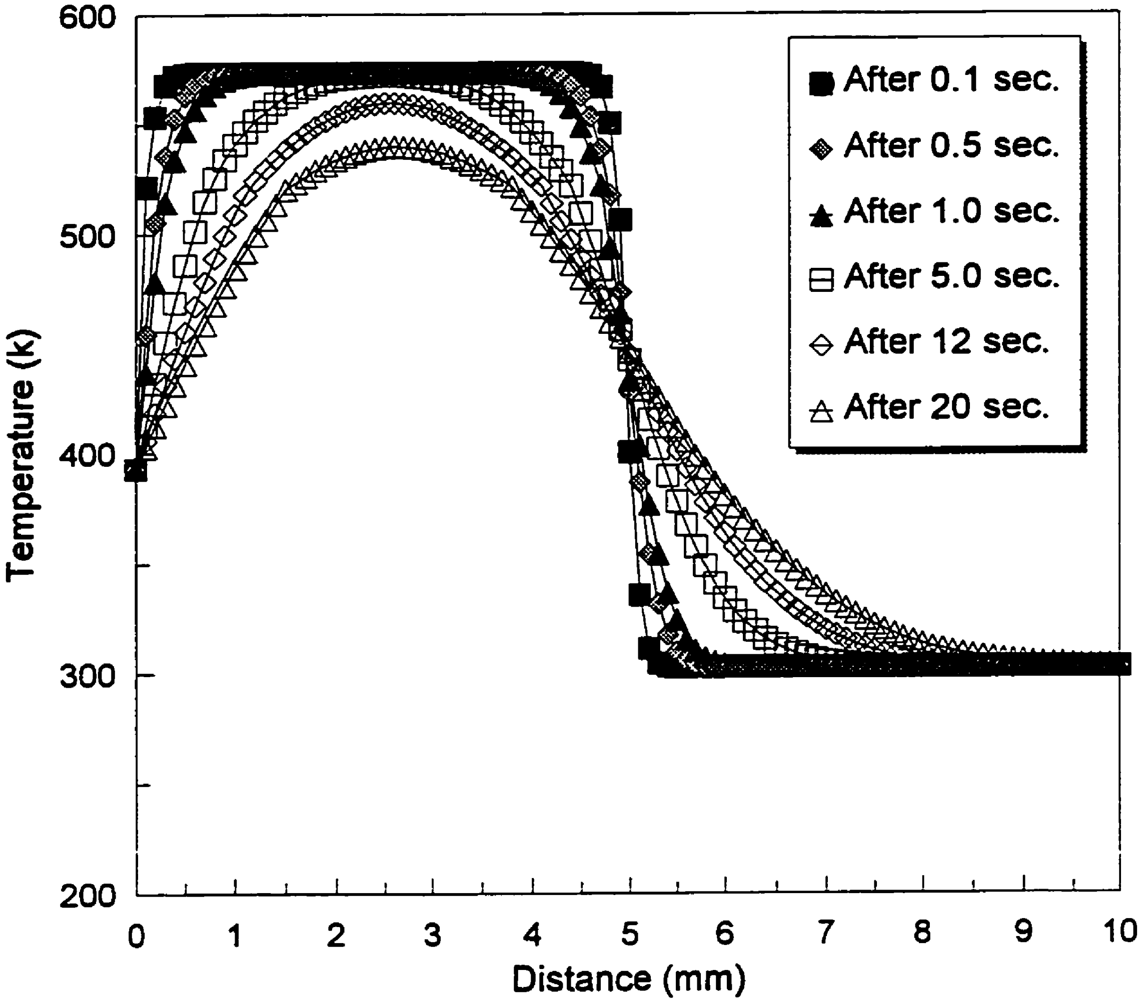

Figure 3.9: Temperature profile at different times in polymer PET, T_w=120°c, $x_s=x_l$

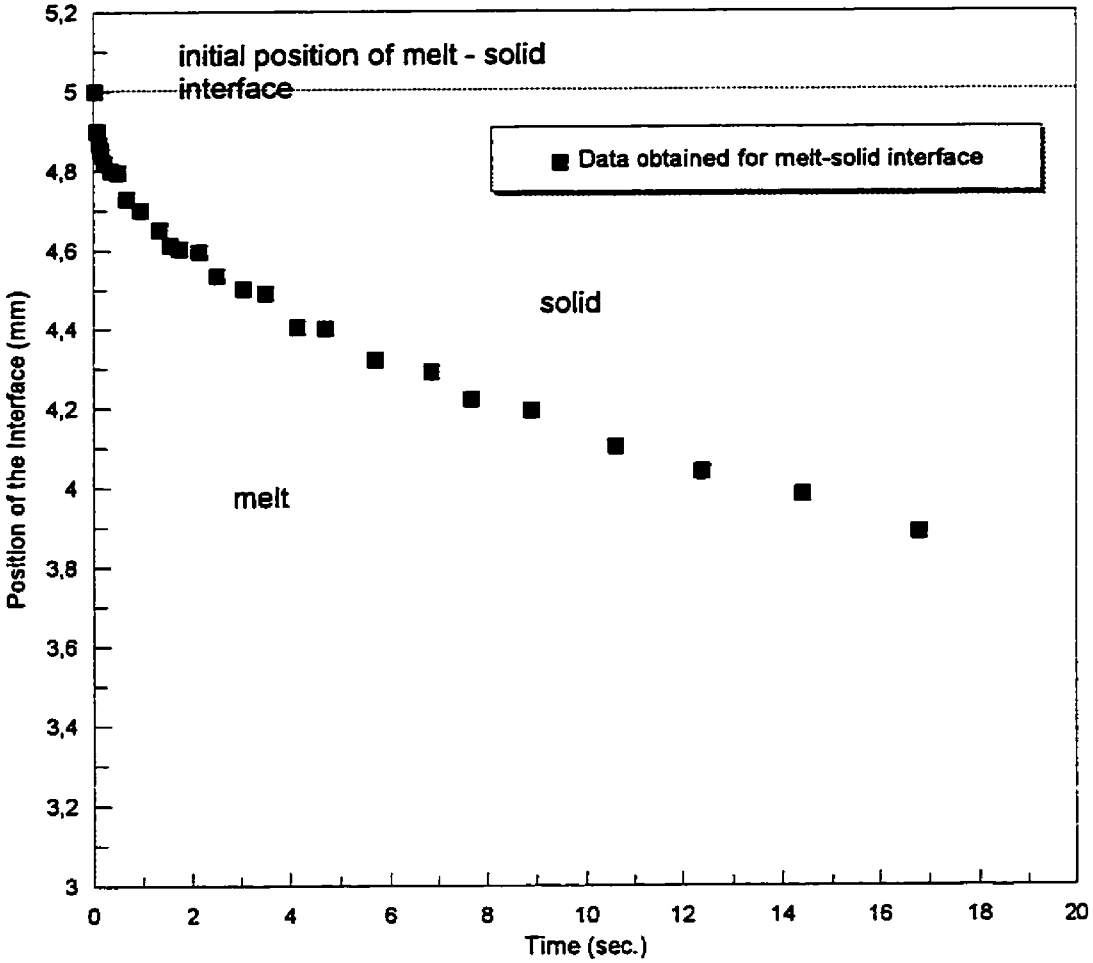

Figure 3.10: Position of melt-solid phase change interface for PET, T_m=250° c, Ti=300° c, T_s=30° c, T_w=100° c, x_s=x_l

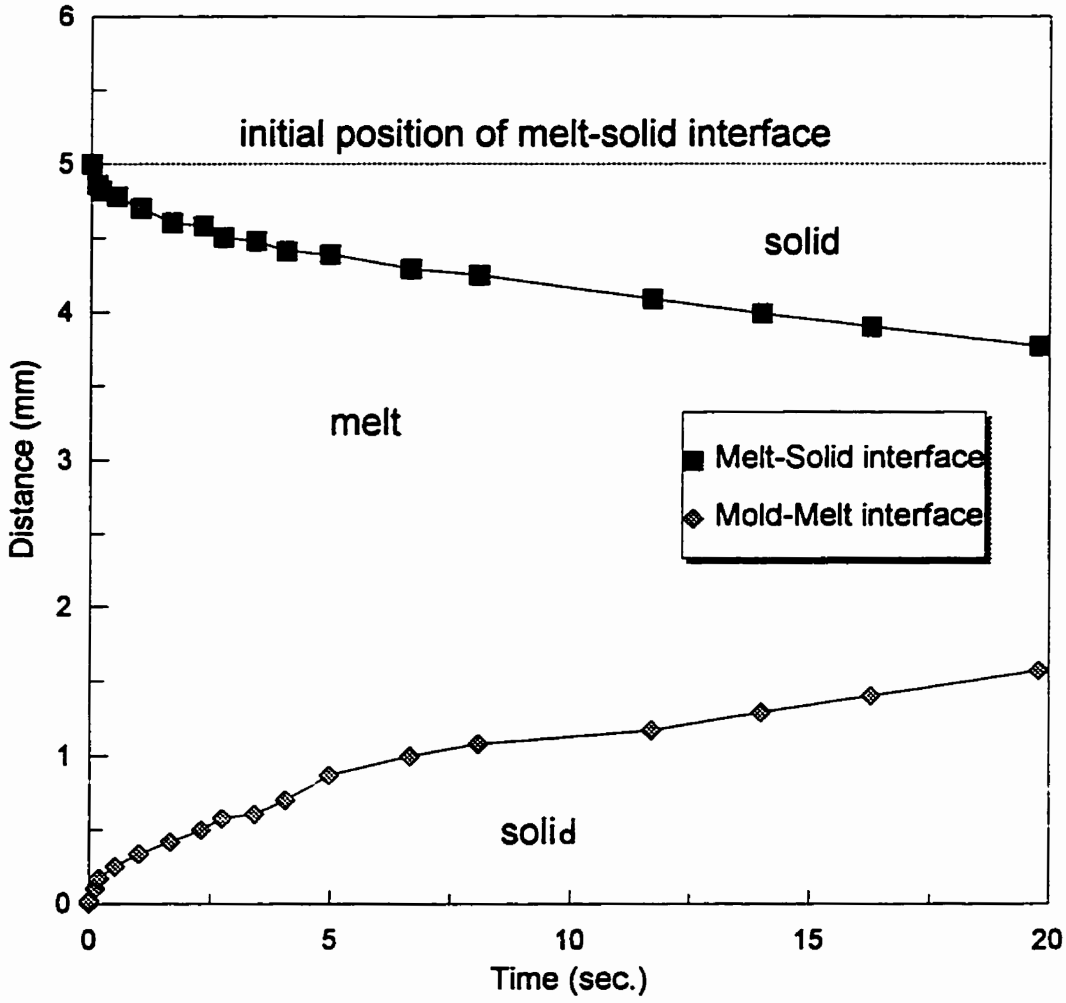

Figure 3.11: Position of melt-solid and mold-melt interfaces for PET, ,T_i=300° c,Ts=30° c,T_w=120° c, x_s=x_l

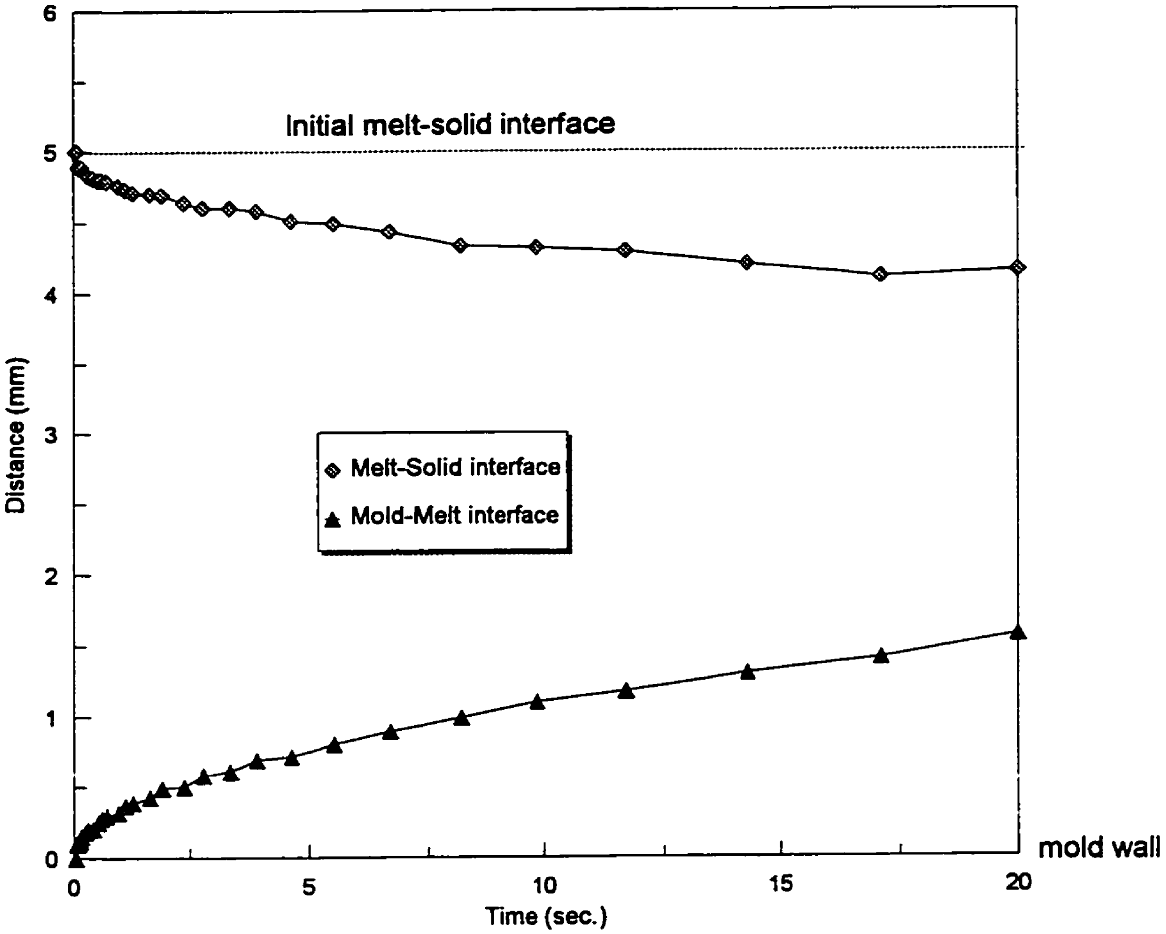

Figure 3.12: Position of melt-solid and mold-melt phase change interface for PET, T_i=300° c, T_s=90° c, T_w=120° c, x_s=x_l

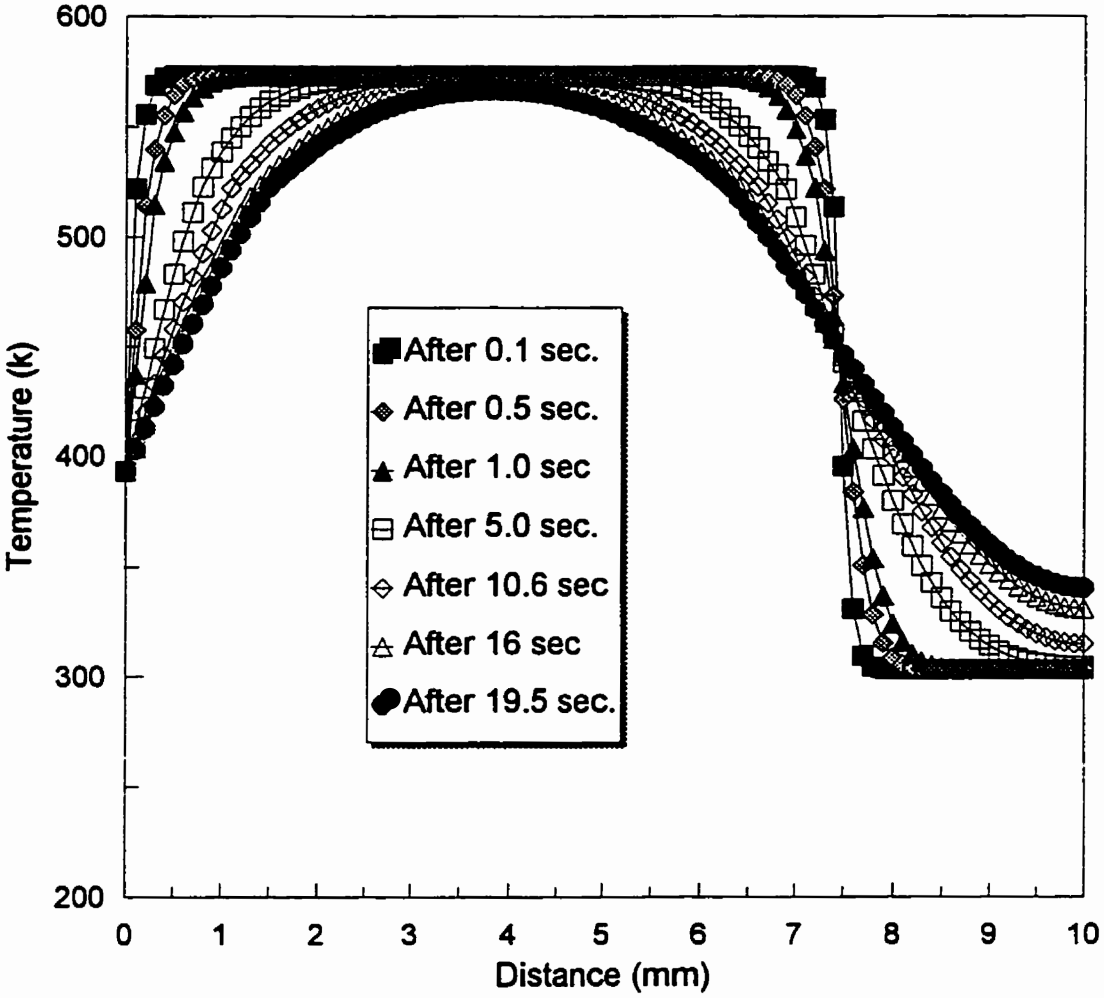

Figure 3.13: Temperature profile at different times for polymer PET, T_w=120°c, x_l=$2x_s$

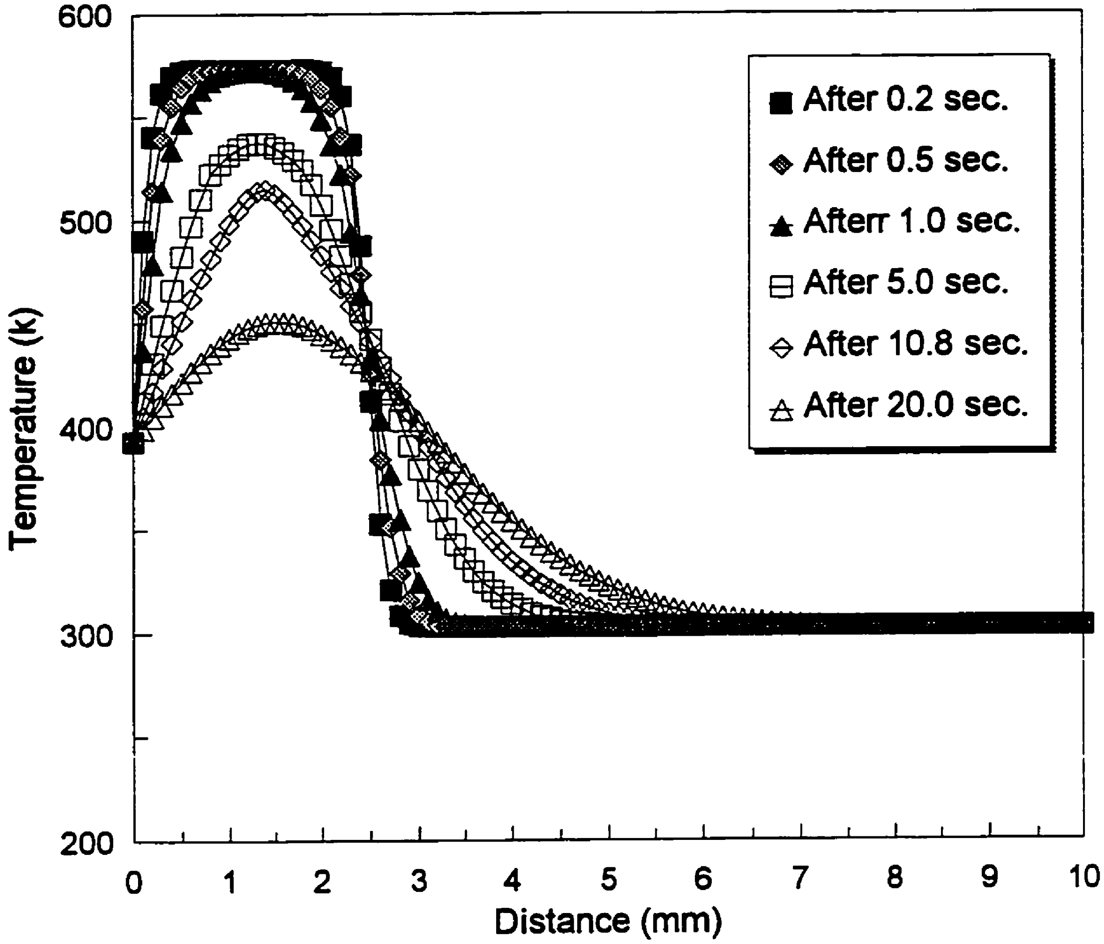

Figure 3.14: Temperature profile at different times for polymer PET, T_w=120°c, $x_s=2x_l$

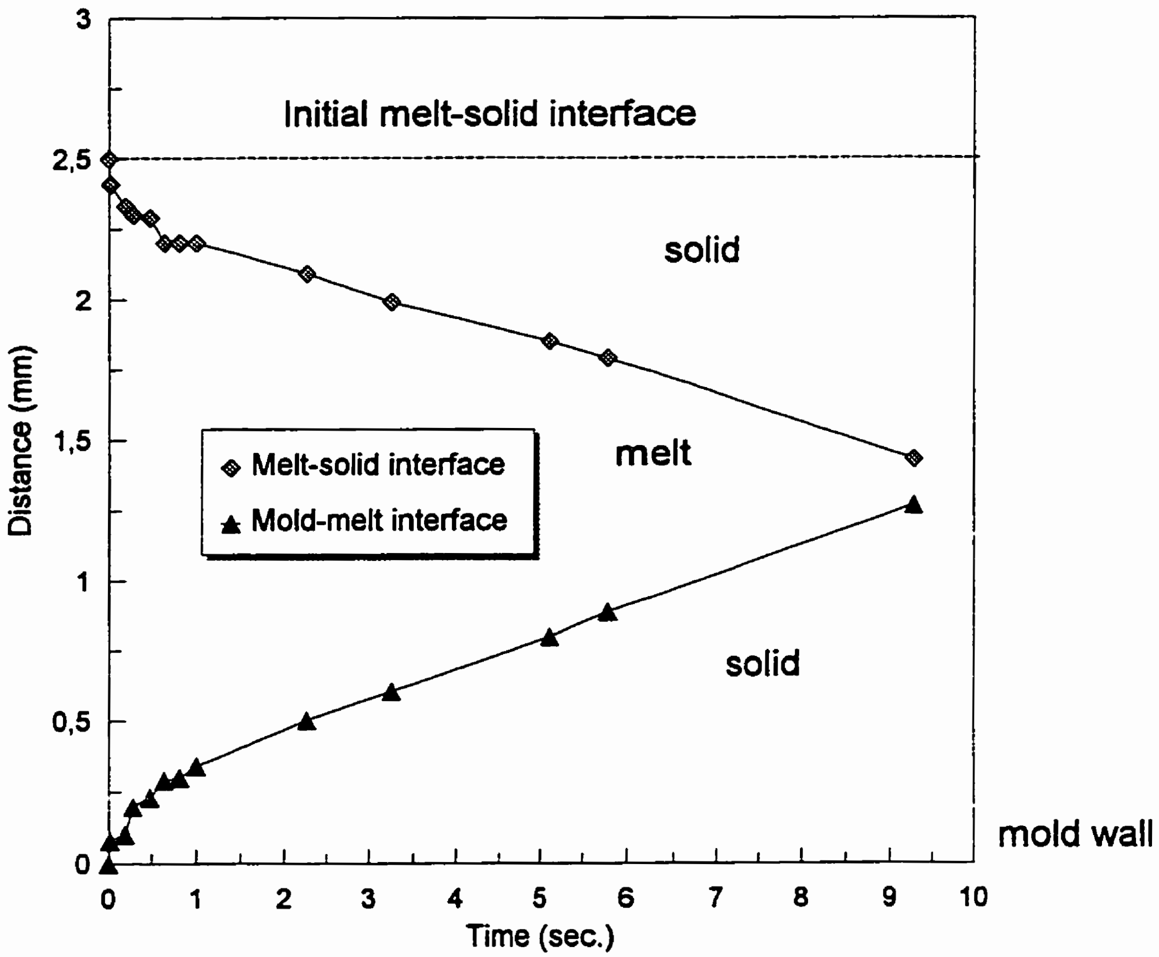

Figure 3.15: Position of melt-solid and mold-melt phase change interface for PET. T_i=300°c, T_w=120°c, T_s=30°c, $x_s=2x_l$

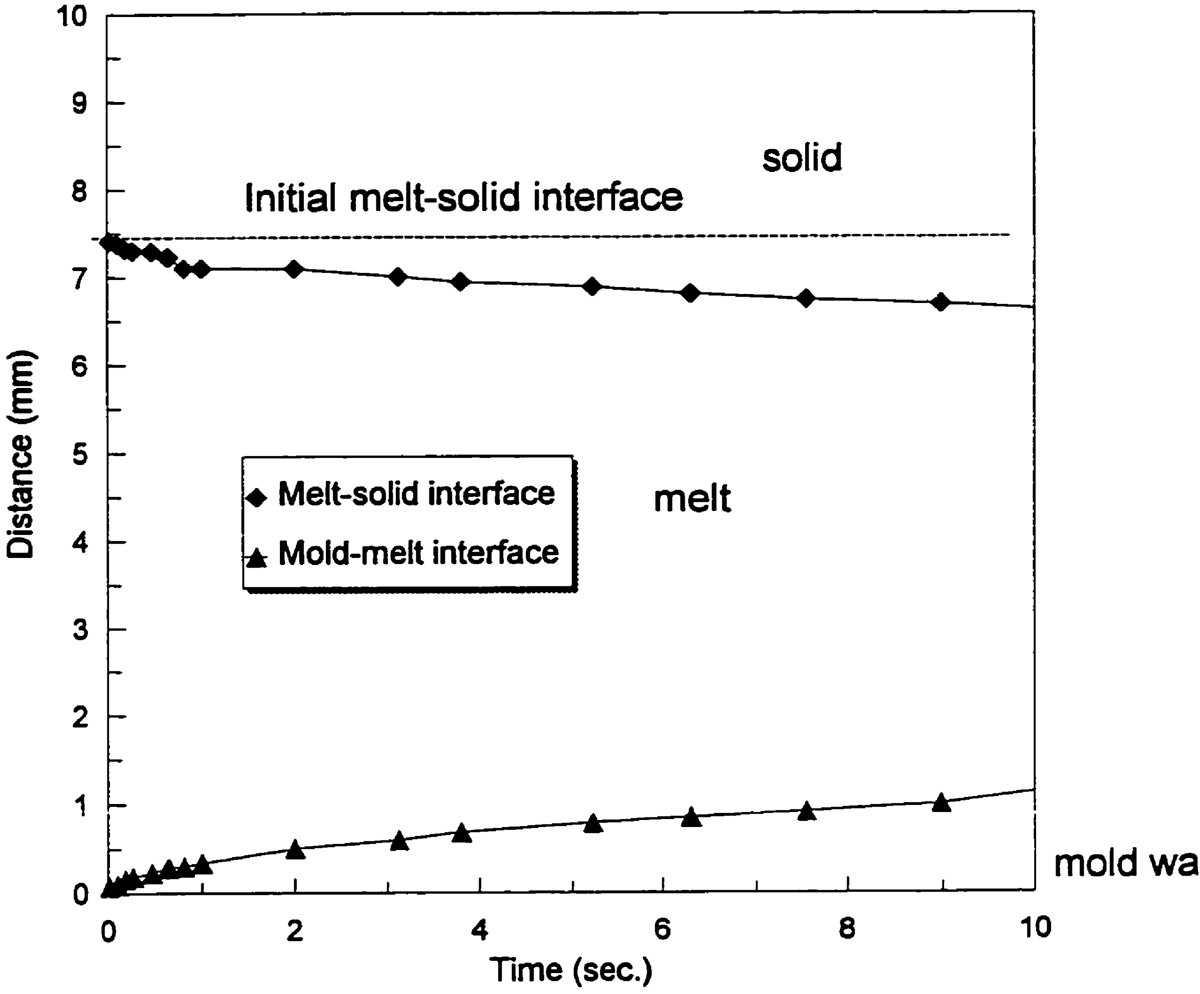

Figure 3.16: Position of melt-solid and mold-melt phase change interface for PET. T_i=300°c, T_w=120°c, T_s=30°c, $x_f=2x_s$

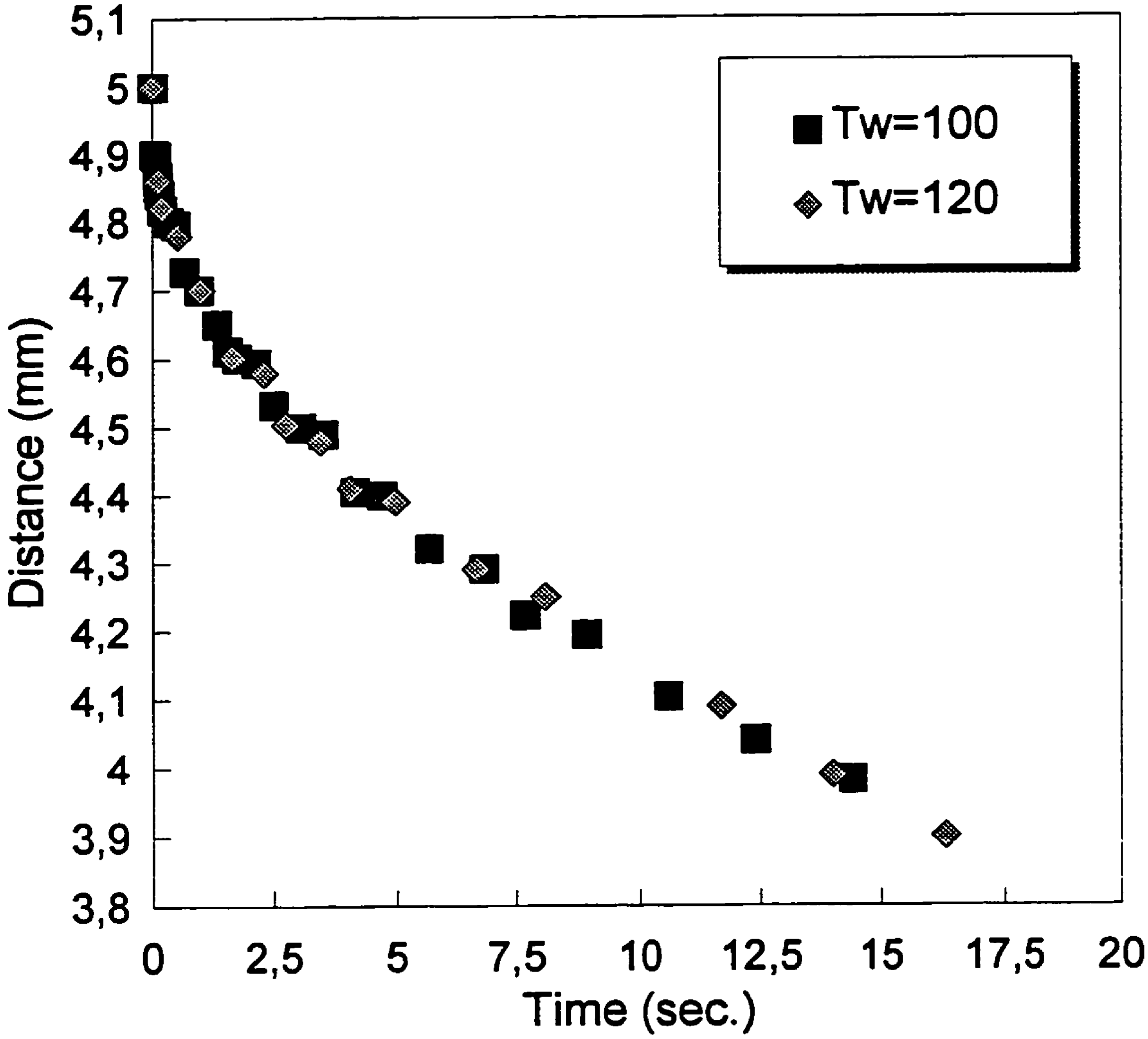

Figure 3.17: Position of melt-solid interfaces of PET for two different wall temperature, T_i=300°c, T_s=30°c, x_s=x_l

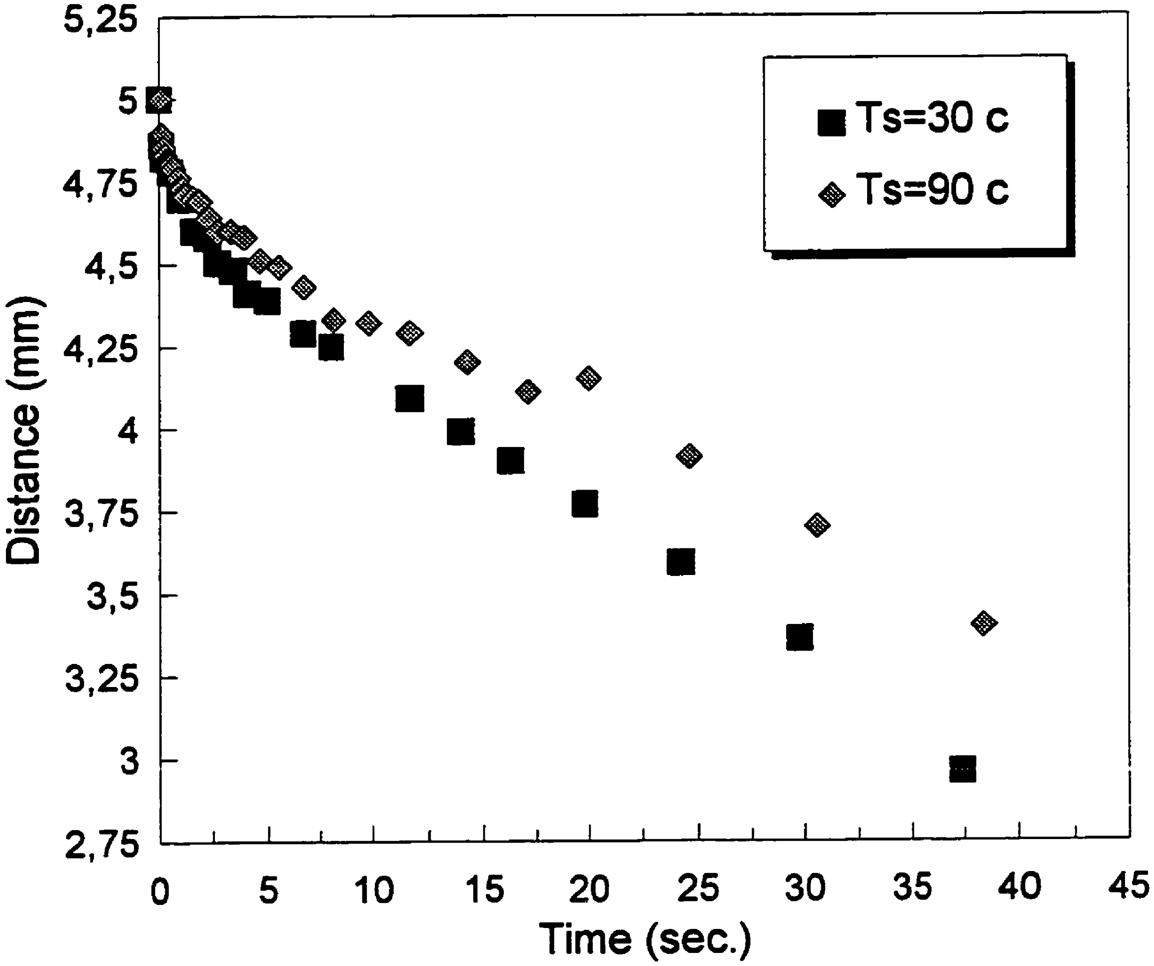

Figure 3.18: Position of melt-solid interface of PET for two different insert temperature, T_i=300°c, T_w=120°c, $x_s=x_l$

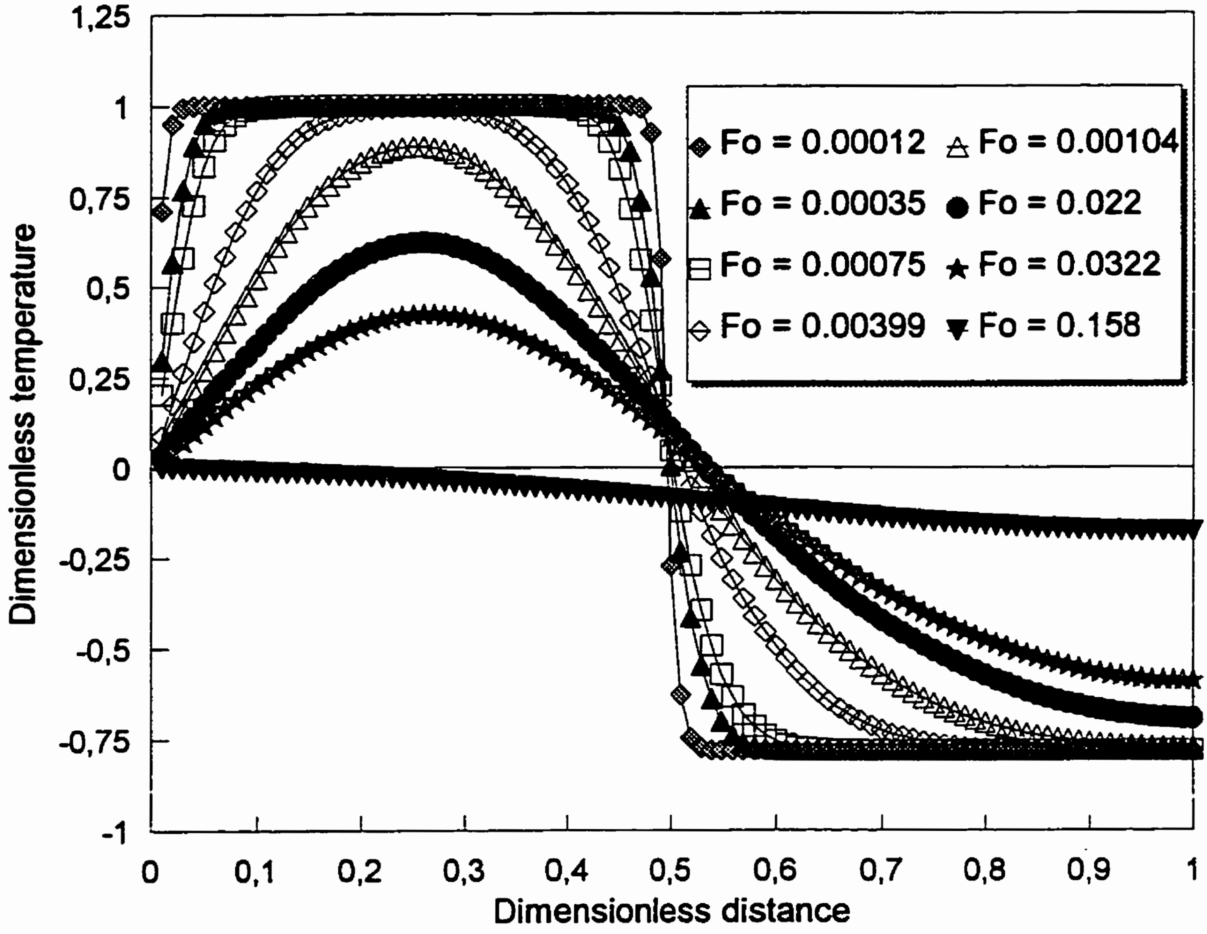

Figure 3.19: Temperature profile at different times for PS, T_w=110°c, T_s=40°c, x_l=x_s

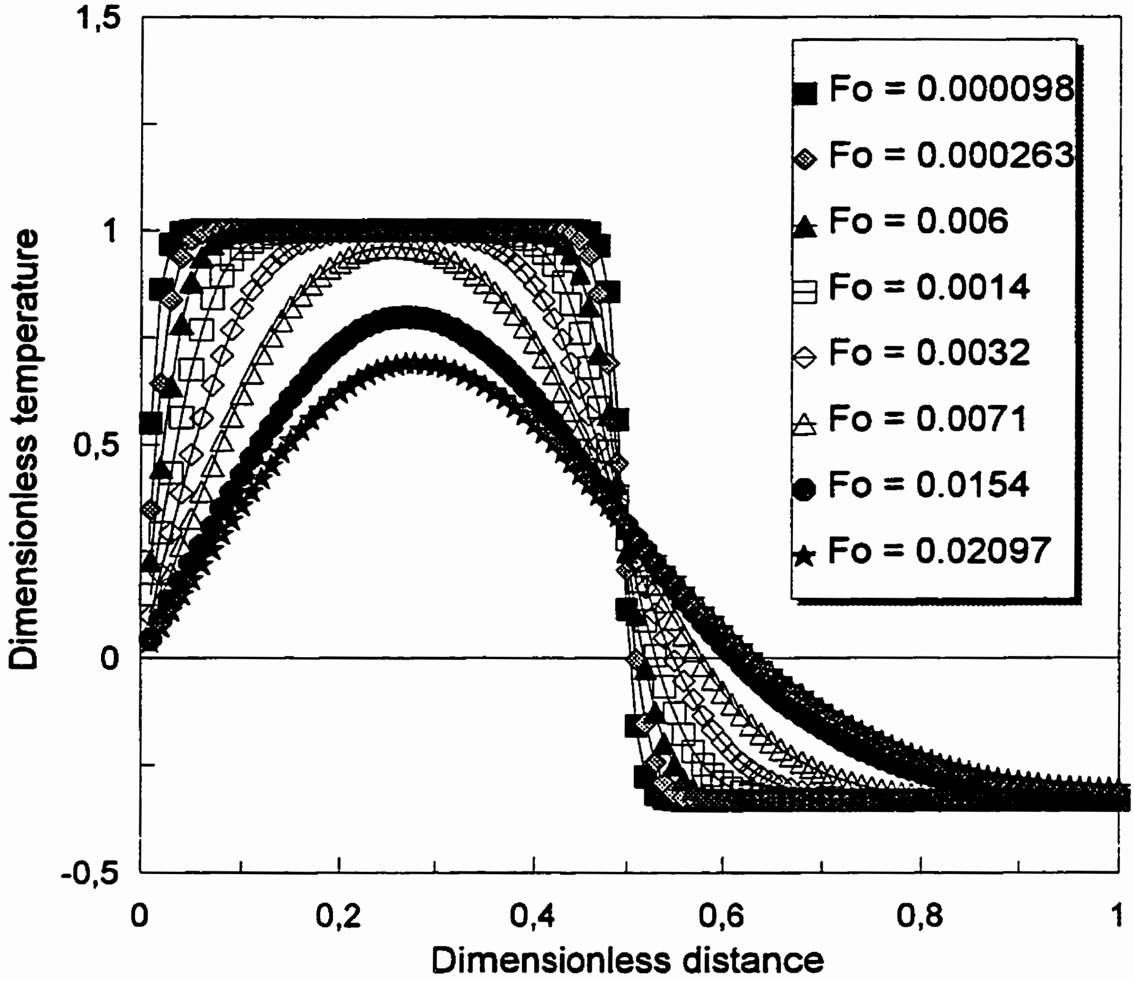

Figure 3.20: Temperature profile at different times for polymer PS, T_w=80°c, T_s=40°c, x_s=x_l

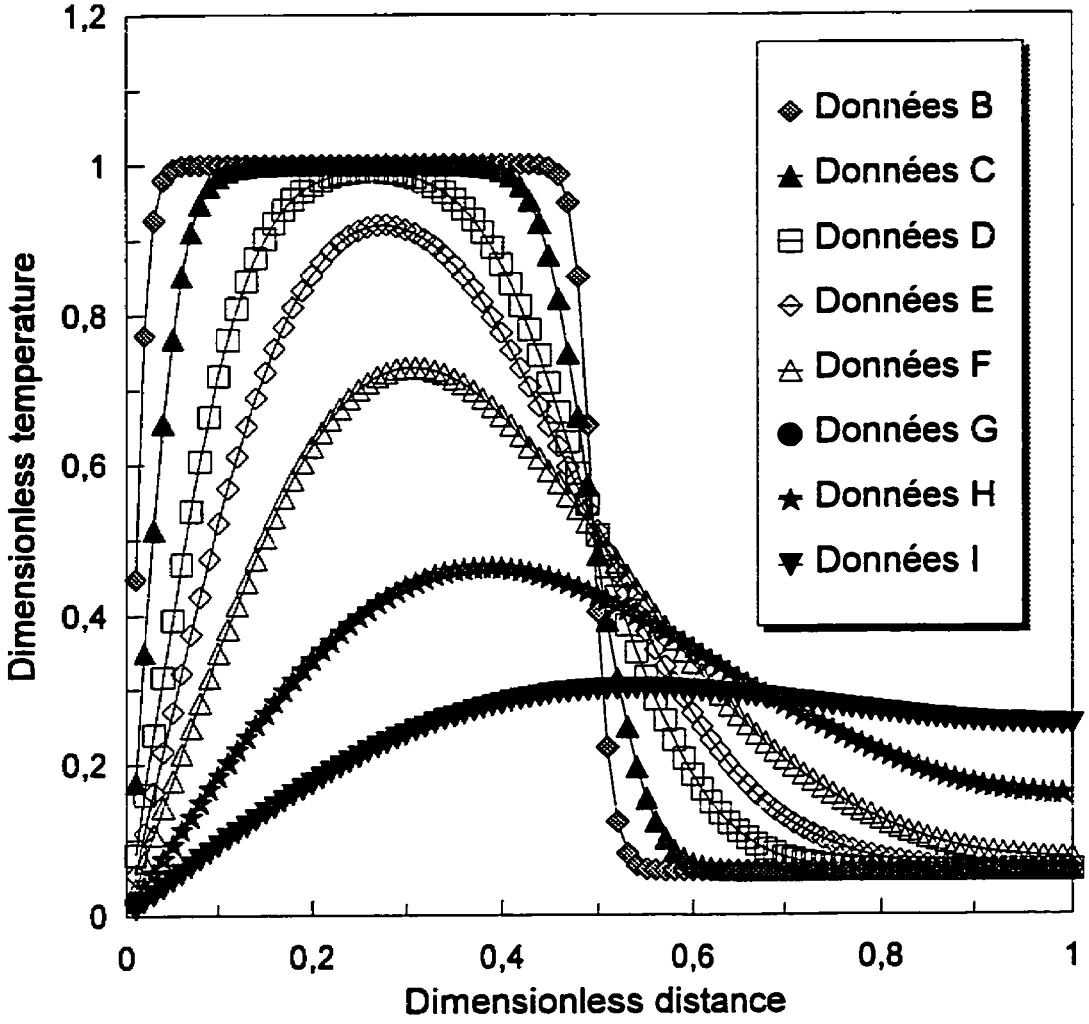

Figure 3.21: Temperature profile at different times for polymer PS, T_w=30°c, T_s=40°c, x_s=x_l

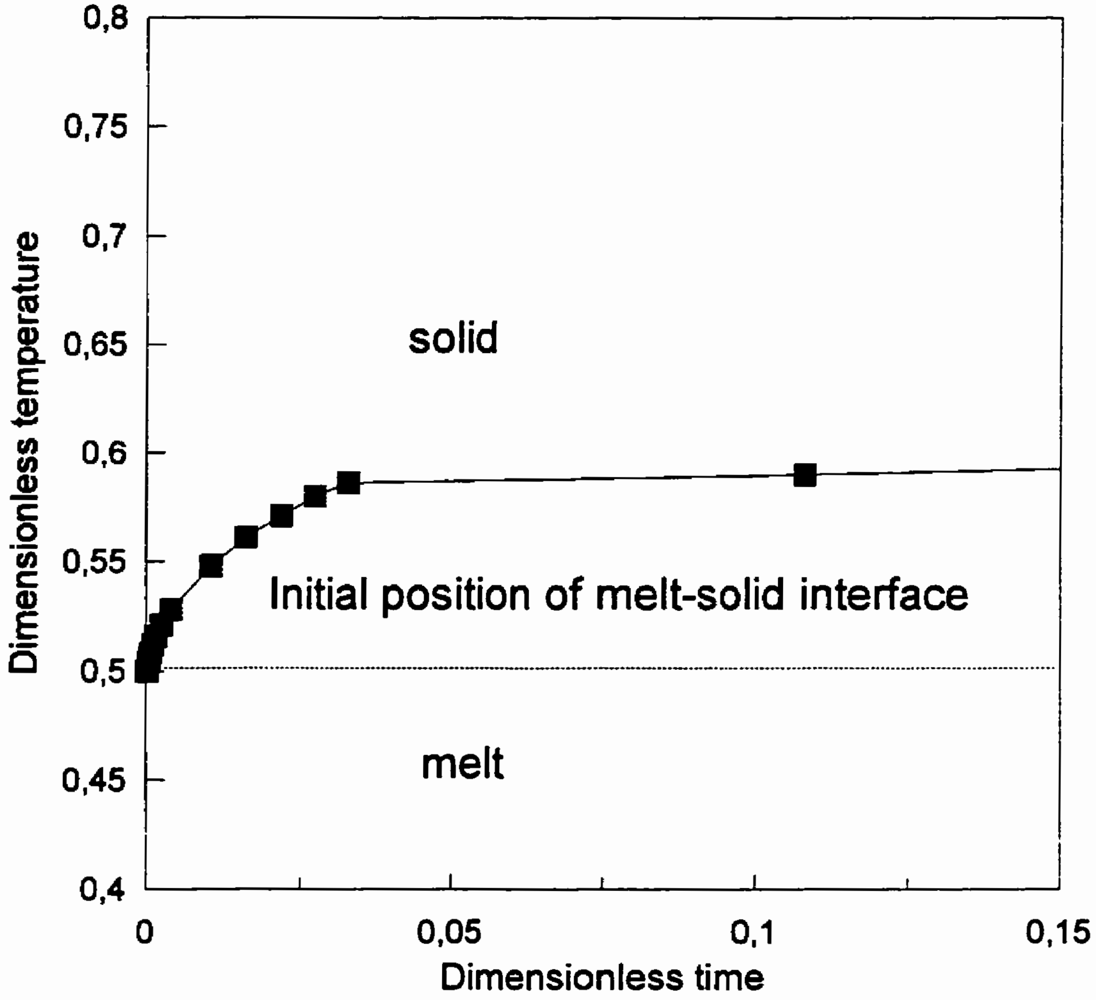

Figure 3.22: Position of melt-solid phase change interface for Polystyrene, T_w=110°c, T_s=40°c, T_l=200°c

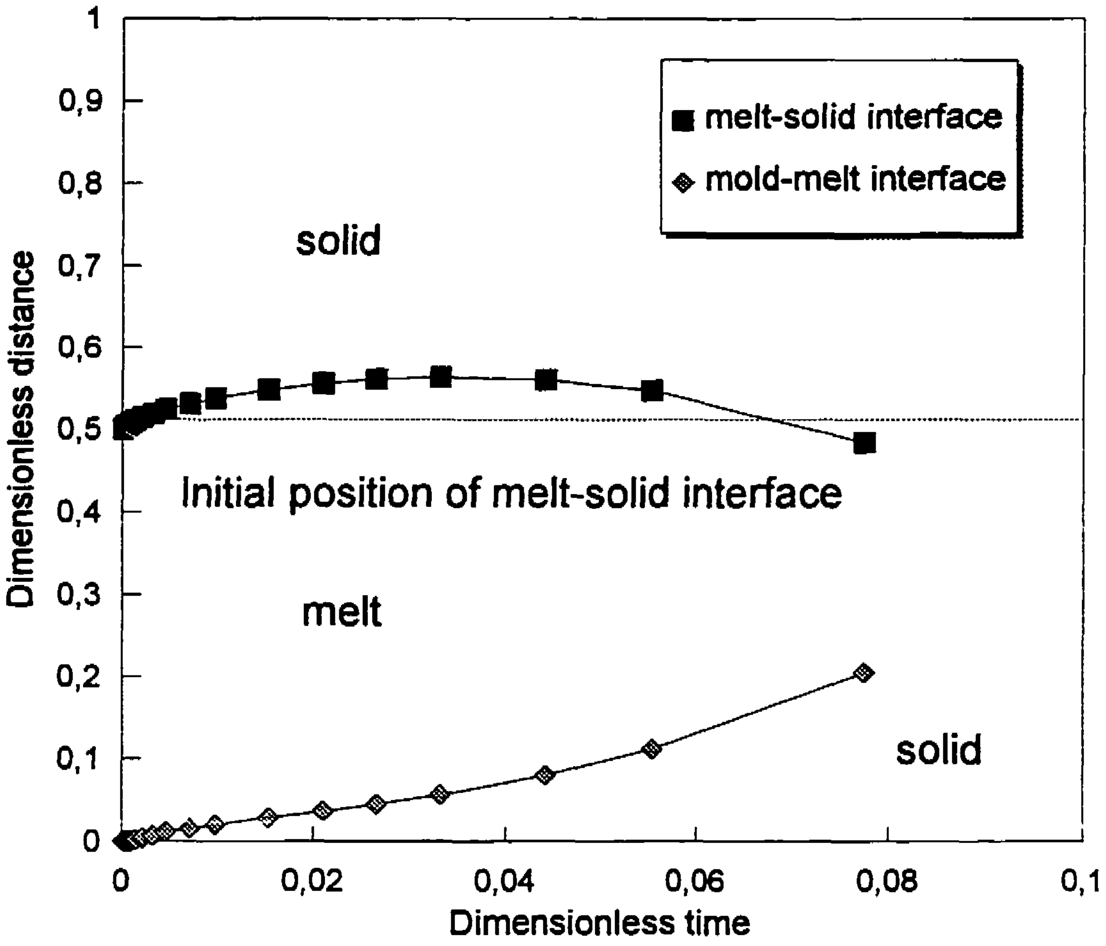

Figure 3.23: Position of melt-solid and mold-melt interface for Polystyrene, T_w=80°c, T_s=40°c, T_l= 200°c

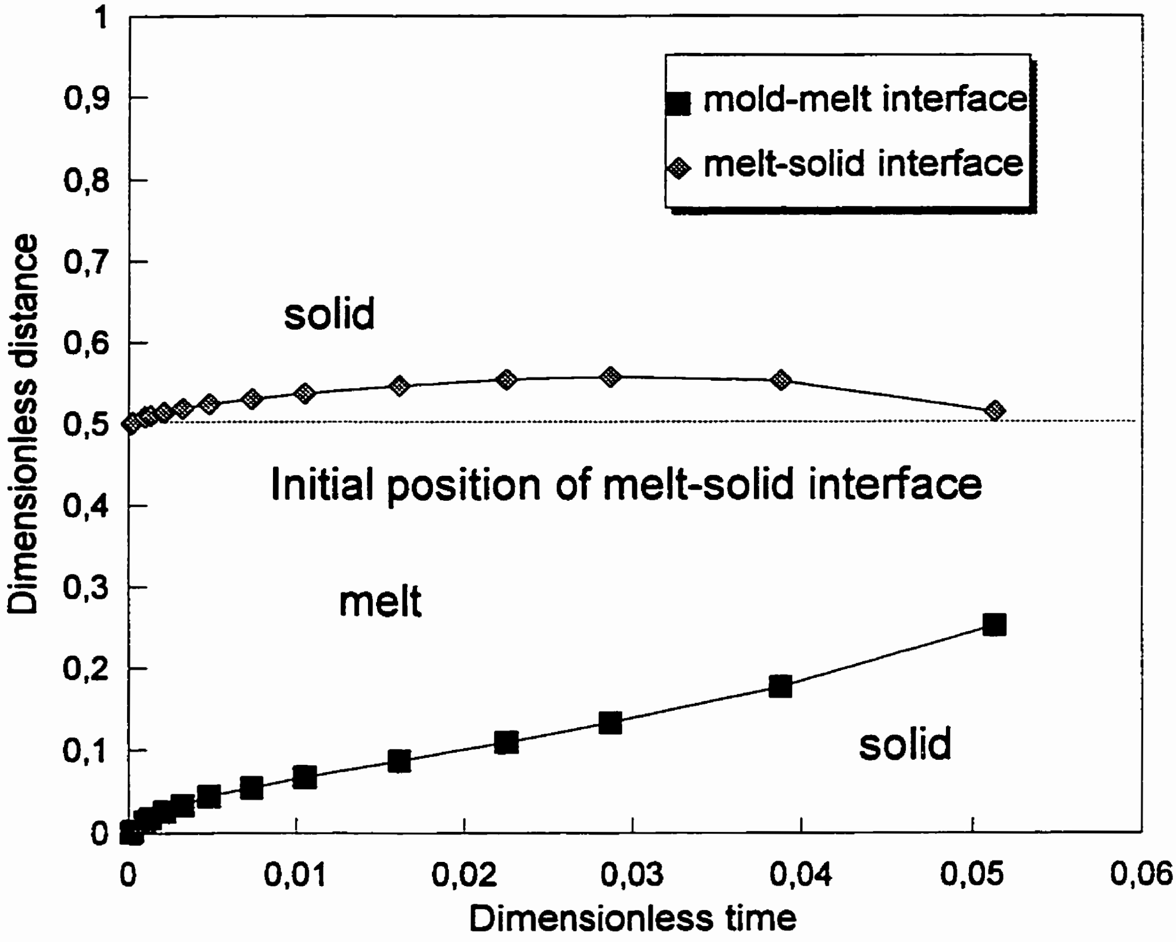

Figure 3.24: Position of mold-melt and melt-solid interface for Polystyrene, T_w= 30°c, T_s=40°c, T_i=200°c, x_s=x_l

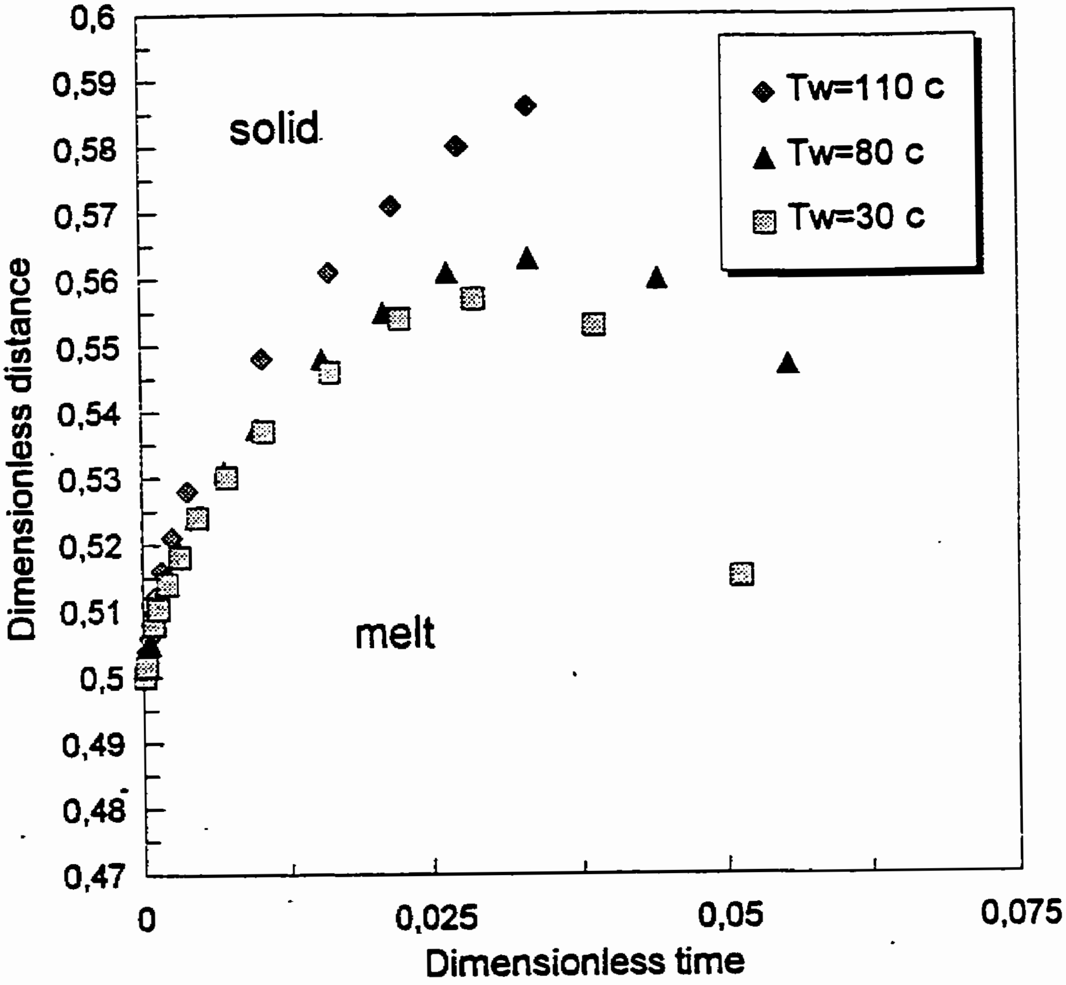

Figure 3.25: Position of melt-solid phase change interface for Polystyrene at different wall temperature

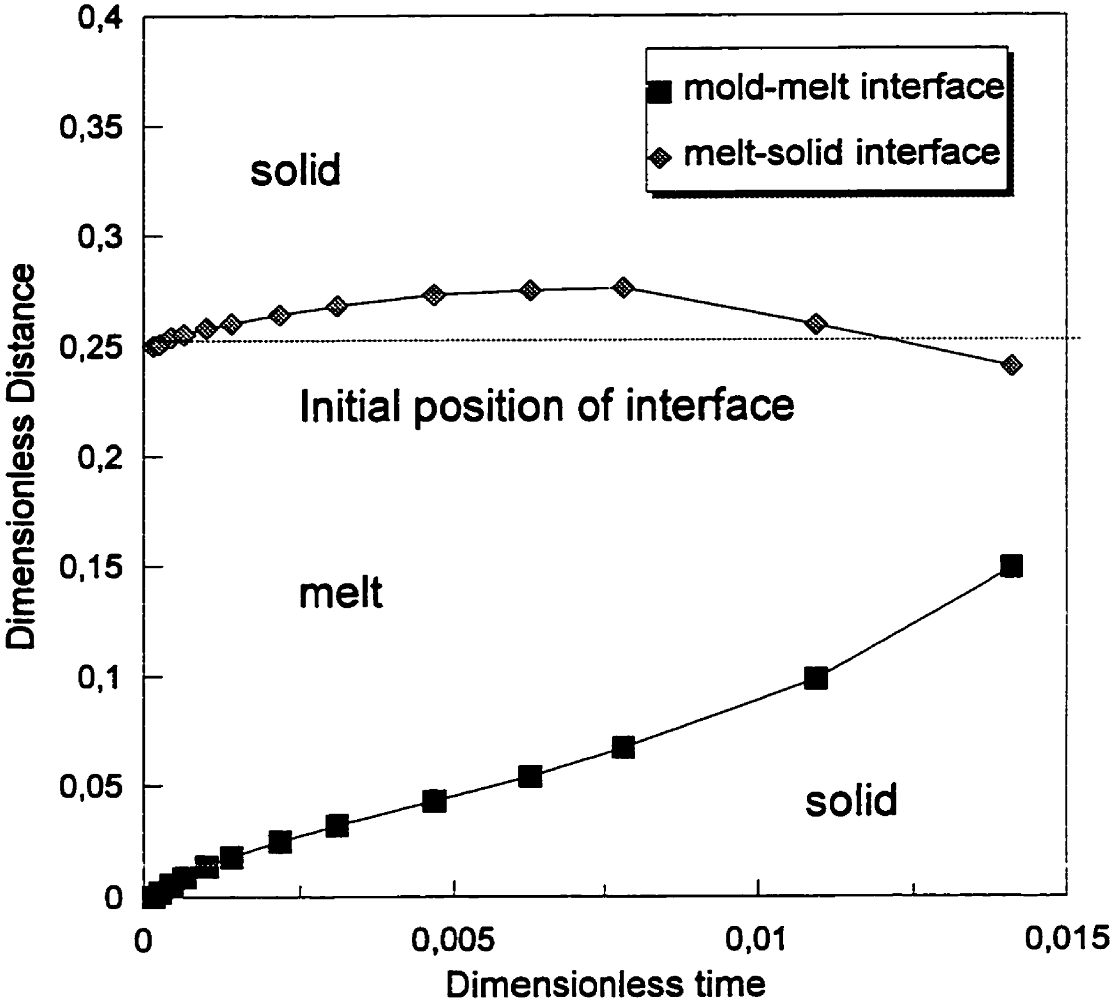

Figure 3.26: Position of mold-melt and melt-solid interface for Polystyrene, T_w=30°c, T_s=40°c, T_l=200°c, x_s=2x_l

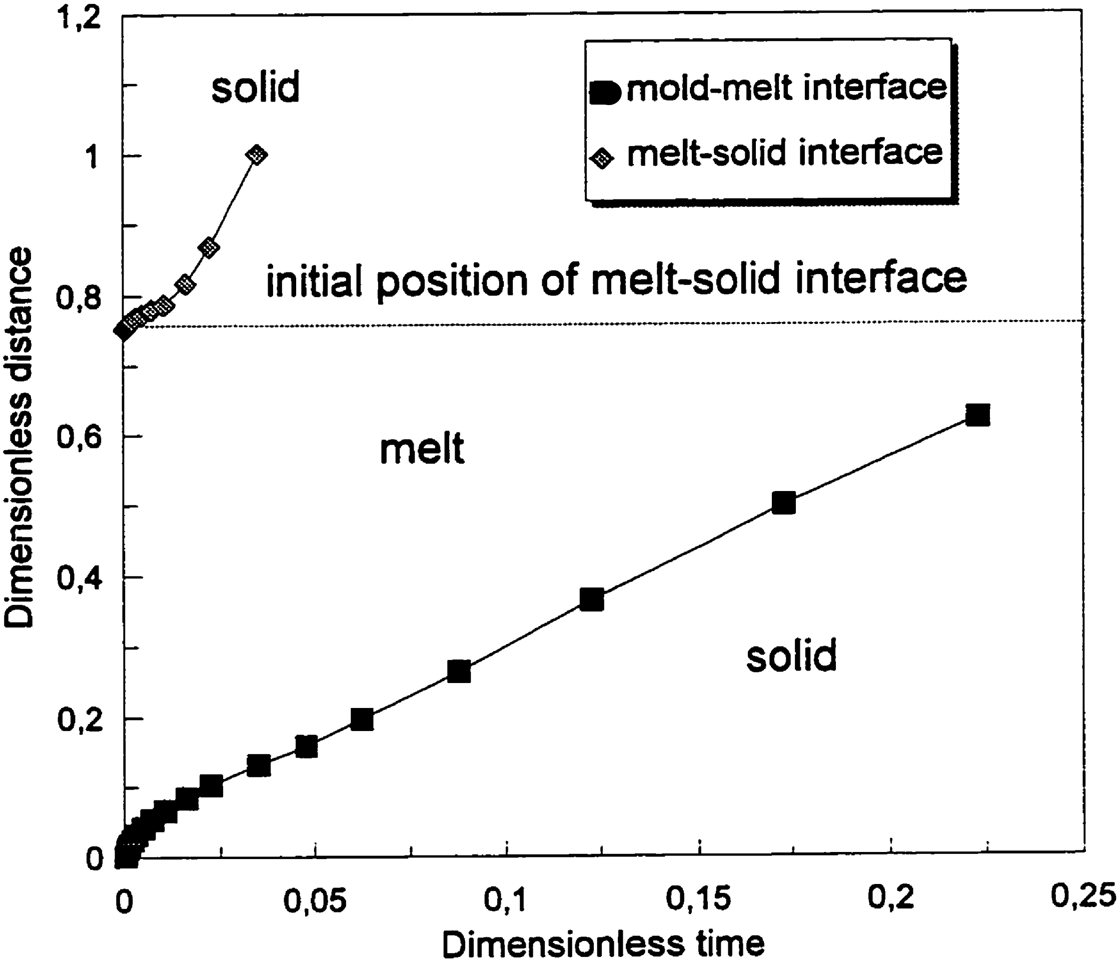

Figure 3.27: Position of mold-melt and melt-solid interface for Polystyrene, T_w=30°c, T_s=40°c, T_l=200°c, $x_l=2x_s$

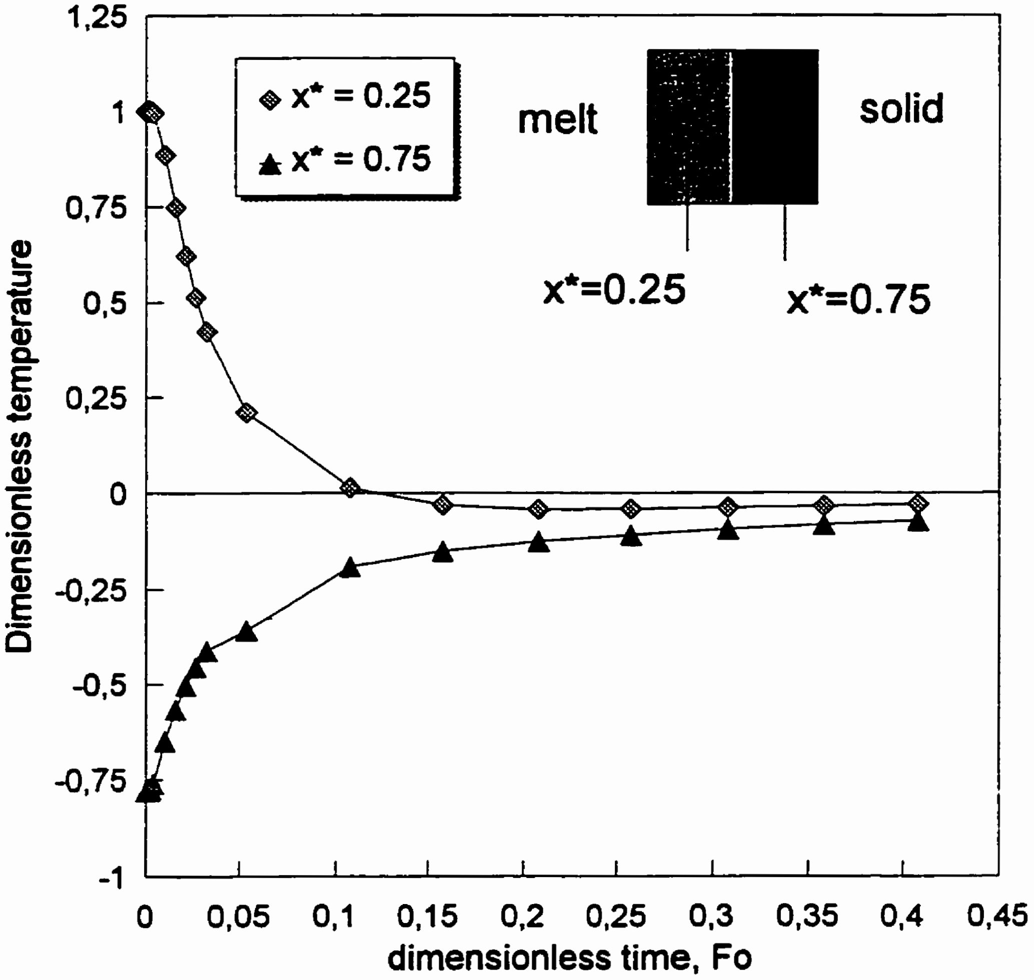

Figure 3.28: Temperature history for x^*=0.25 and x^*=0.75, in melt and solid respectively.Polystyrene, T_w=110°c, x_s=x_l

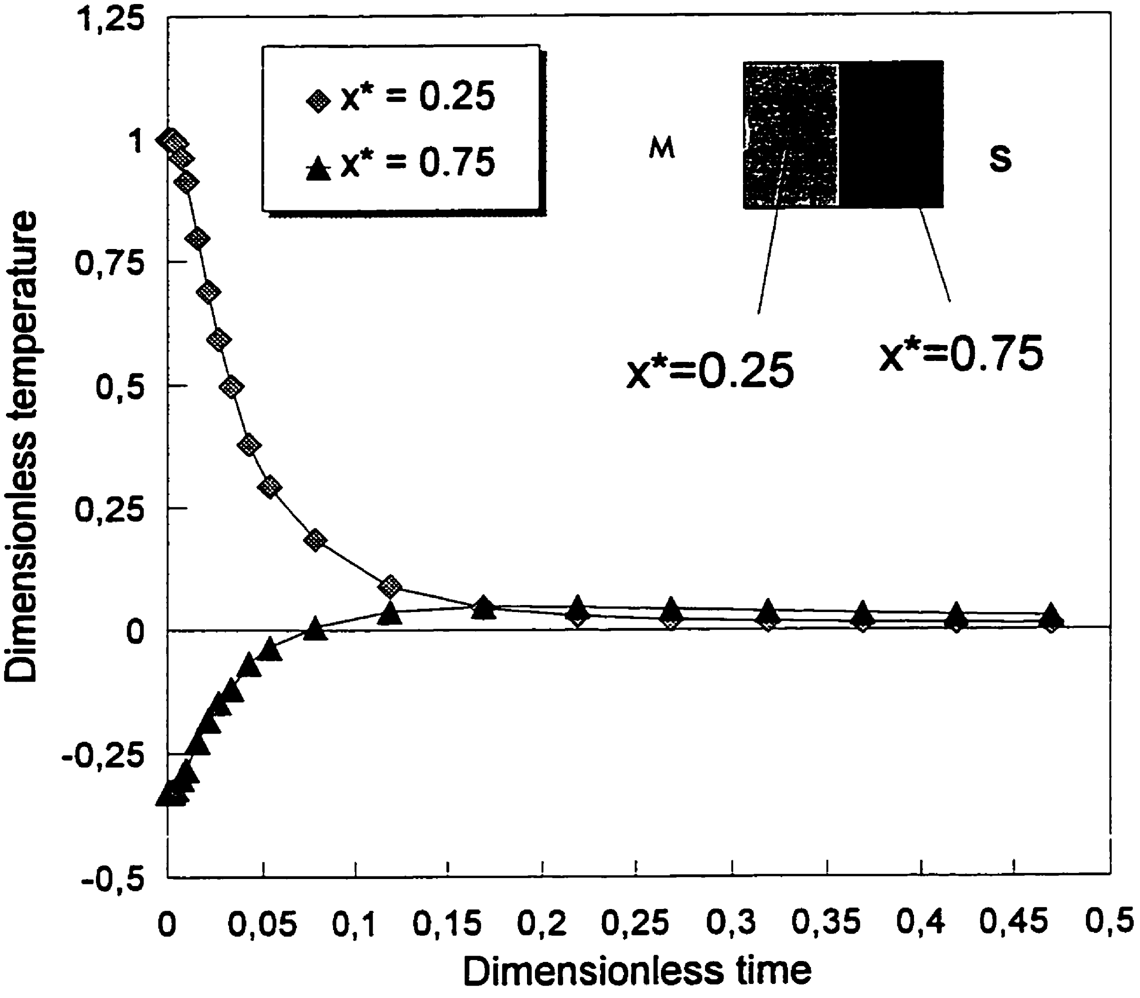

Figure 3.29: Temperature history for $x^*=0.25$ and $x^*=0.75$, in melt and solid respectively. Polystyrene, $T_w=80°c$, $x_s=x_l$

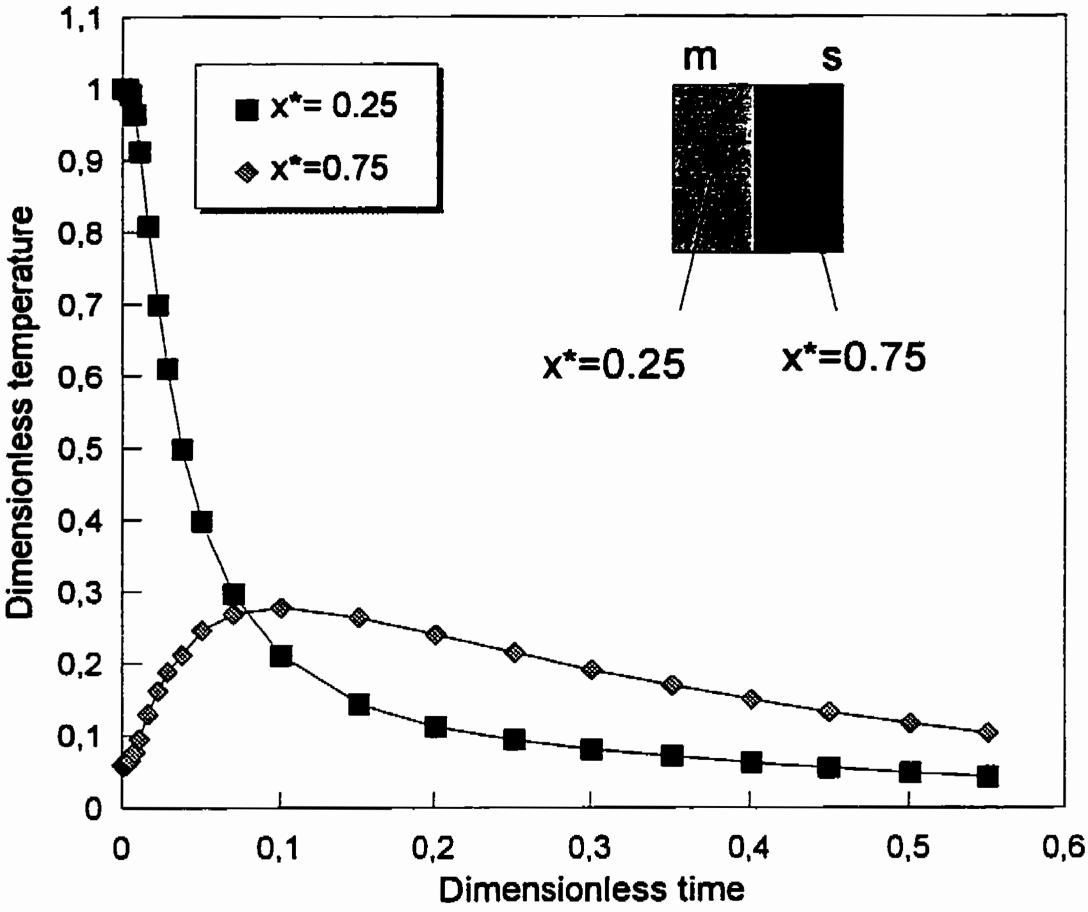

Figure 3.30: Temperature history for x*=0.25 and x*=0.75, in melt and solid respectively. T_w=30°c, $x_l=x_e$

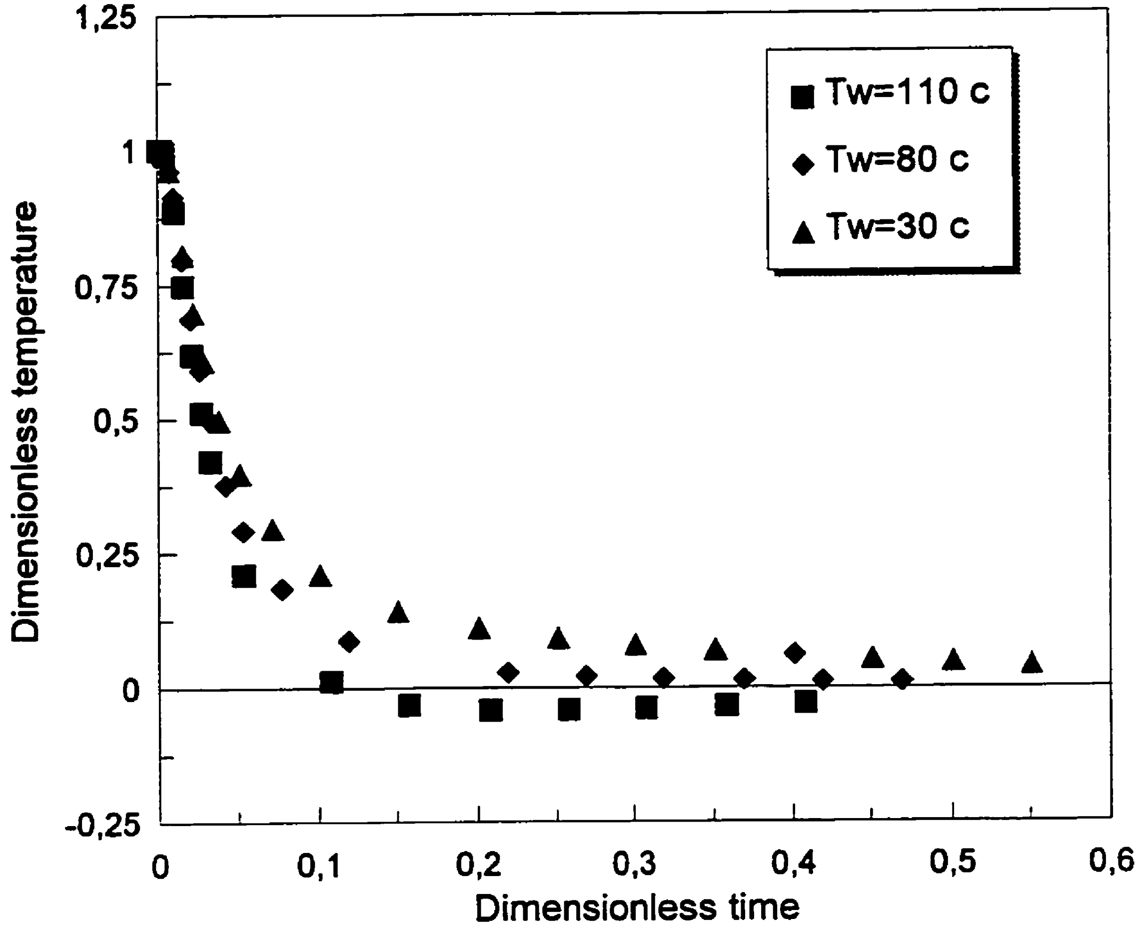

Figure 3.31: Temperature history for x*=0.25 in melt, for three different wall temperatures

CONCLUSION

As we can see from the results the solution to the heat transfer equations is largely controlled by the boundary conditions used to specify the problem. Different parameter regimes induce possible scenarios of rapid initial melting or freezing and the melt front may then grow or decay to a limiting value as steady state develops. The resulting heat transfer process may progress in many different ways dictated by the parameters involved in the system. The initial velocity of melt front may have negative or positive influence on the melting or freezing. For different temperature systems, the initial motion of melt-solid interface remains the same. Since the solid and melt are finite, large time steady state solution are possible. They are dependent in the thermal parameters of the process.

In the case of melting of the solid insert, a limiting position of melt-solid interface can be detected. This limiting position depends on the mold temperature. The higher the temperature difference between the mold and the melt, the lower is the penetration depth of front in the solid insert. The front positions is not disturbed by mold temperature at short times, however long time solution can be highly affected by this boundary condition. For long times the temperature difference between melt and mold wall controls the heat transfer rate of the system. Also it should be mentioned here that this heat transfer rate depends on the nature of contact between mold and melt polymer, this effect should be considered for longer times. The limiting position of the front is also controlled by initial thickness ratio, X. If the liquid region is relatively large the process may be terminated when the cold body melts completely leaving purely liquid or conversely, if the liquid region is small it may freeze completely leaving purely solid. The exact conditions depend on the specific polymer under consideration. By altering the value of X, while holding the other parameters fixed, the initial motion of the boundary remains the same, but the steady state solution can be varied to literally any position across the spatial region.

The freezing mechanism of melt at the mold wall, in its early stages is similar to the one obtained for semi-infinite medium by Stefan. The reason for this similarity is the low thermal conductivity of the polymer melt, resulting in a shallow penetration depth of heat transfer. The agreement is good for short times. For longer times, the difference between numerical results and Stefan solution is more sensible which is because of the difference between the nature of the two problems.

The rate of melt-solid interface penetration for semi-crystalline polymers (PET) is lower than amorphous polymers (PS). When a semi-crystalline polymer changes from melt to solid state or vice versa, a latent heat of fusion must be added during melting or taken away during cooling which causes a delay in temperature range. When we define a freezing range, instead of a complete delay of temperature when the upper range is reached, only a partial delay proportional to the crystallization fraction is applied. The partial delay in the temperature reduction is terminated when the lower limit of the freezing range is obtained. Generally the heat required to melt semi-crystalline plastics at a given temperature exceed those of amorphous at the same temperature.

We analyzed the problem by assuming that in a pure material, the solid and liquid phases are separated by smooth and continuos interface. In general, however, the interface is irregular in shape and is an unknown function in space and time.

For crystalline polymers, the effect of crystallinity has not been accounted for. There has been much recent activity in trying to predict the microstructure from the solidification analysis, one of the difficulties has been that the process dynamic controls the temperature at which phase change takes place. Although we can not find a precise method to analyze this problem, latent heat control of phase change problem seems to give very good first approximation to the front position. However, this aspect should be studied in more detail.

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APPENDIX I

Appendix I

Changes of Heat Capacity of Polymers with Temperature

Van Krevelen, by examining available literature data, shows that, for all polymers investigated, the curves for the molar heat capacity of solid and liquid may be approximated by straight lines, except for the solid below 150K. So if the slopes of these lines are known, the heat capacity at an arbitrary temperature may be calculated approximately from its value at 298K. For a number of polymers the slopes of the heat capacity curves, related to the heat capacity at 298K, are given. The slopes of the heat capacity lines for solid polymers show a mean value;

$$\frac{1}{C_p^{\,s}(298)}\frac{dC_p^{\,s}}{dT} = 3\times10^{-3} \qquad \text{(A1-1)}$$

For liquid polymers, an analogous experiment may be used. But much larger deviations occur. In this case;

$$\frac{1}{C_p^{\,l}(298)}\frac{dC_p^{\,l}}{dT} = 1.2\times10^{-3} \qquad \text{(A1-2)}$$

With a mean deviation of 30%. However if experimental data is lacking, the temperature function of the heat capacity may be approximated with these mean values, so that;

$$\begin{aligned} C_p{}^s(T) &= C_p{}^s(298)[1+3\times10^{-3}(T-298)] = C_p{}^s(298)[0.106+3\times10^{-3}T] \\ C_p{}^l(T) &= C_p{}^l(298)[1+1.2\times10^{-3}(T-298)] = C_p{}^l(298)[0.64+1.2\times10^{-3}T] \end{aligned} \quad \text{(A1-3)}$$

C_p = molar heat capacity

The molar heat capacity is the specific heat multiplied by the molar mass (the molar mass of a structural unit in the case of polymers).

With the aide of these equations specific heat capacity in the solid and the liquid state at temperatures of practical interest may be predicted approximately from their values at room temperature. The ratio of $C_p^l(298)/C_p^s(298)$ shows a mean deviation of 7% from the mean value calculated from available experimental data for different polymers.

The linear approximations of the curves for C_p^s and C_p^l as a function of temperature may be used for estimating C_p^l and C_p^s at the melting point. The ratio C_p^l/c_p^s at the melting point shows a mean deviation of 6% from the mean value calculated from experimental data for different polymers.

APPENDIX II

Appendix II

Neumann's Solution for Melting and Solidification in one Dimension

Solidification in a half-space (two-phase problem).

A liquid at a uniform temperature T_i that is higher than the melting temperature T_m of the solid phase is confined to a half -space x>0. At time t=0 the boundary surface at x=0 is lowered to a temperature T_w below T_m and maintained at that temperature for times t>0. As a result, the solidification starts at the surface x=0 and the solid-liquid interface moves in the positive x direction. This problem is a two-phase problem because the temperatures are unknown in both the solid and liquid phases. In the following analysis we determine the temperature distributions in both phases and the location of the solid-liquid interface. This problem is more general than the ones considered in the previous examples; its solution is known as Neumann's solution.

Solution

The mathematical formulation of this problem for the solid phase is given as;

$$\frac{\partial^2 T_s}{\partial x^2} = \frac{1}{\alpha_s}\frac{\partial T_s(x,t)}{\partial t} \qquad \text{in} \qquad 0 < x < s(t), \quad t > 0 \qquad (A2-1)$$

$$T_s(x,t) = T_w \qquad \text{at} \qquad x = 0, \qquad t > 0 \qquad (A2-2)$$

For the liquid phase as;

$$\frac{\partial^2 T_l}{\partial x^2} = \frac{1}{\alpha_l}\frac{\partial T_l(x,t)}{\partial t} \qquad \text{in} \qquad s(t) < x < \infty, \quad t > 0 \qquad (A2-3)$$

$$T_l(x,t) \rightarrow T_i \qquad \text{as} \qquad x \rightarrow \infty, \qquad t > 0 \qquad (A2-4)$$

$$T_l(x,t) = T_i \qquad \text{for} \qquad t = 0, \qquad x > 0 \qquad (A2-5)$$

And the coupling condition at the interface x=s(t) as;

$$T_s(x,t) = T_l(x,t) = T_m \qquad \text{at} \qquad x = s(t), \quad t > 0 \qquad (A2-6)$$

$$k_s\frac{\partial T_s}{\partial x} - k_l\frac{\partial T_l}{\partial x} = \rho L\frac{ds(t)}{dt} \qquad \text{at} \qquad x = s(t), \quad t > 0 \qquad (A2-7$$

If swe choose a solution for $T_s(x,t)$ in the form

$$T_s(x,t) = T_w + A\,erf[x/2(\alpha_s t)^{1/2}] \qquad (A2-$$

$$T_l(x,t) = T_i + B\,erf[x/2(\alpha_l t)^{1/2}] \qquad (A2-$$

The differential equation and the boundary condition are satisfied. The constants A and B are yet to be determined. Equations (A2-8) and (A2-9) are introduced into the interface condition (A2-6). We find;

$$T_w + A\,erf(\lambda) = T_i + B\,erfc\,[\lambda(\frac{\alpha_s}{\alpha_l})^{1/2}] = T_m \qquad (A2-10)$$

Where;

$$\lambda = \frac{s(t)}{2(\alpha_s t)^{1/2}} \qquad or \qquad s(t) = 2\lambda(\alpha_s t)^{1/2} \qquad (A2-11)$$

The coefficient A and B are determined from equations (A2-11) as;

$$A = \frac{T_m - T_w}{erf(\lambda)}, \qquad B = \frac{T_m - T_i}{erfc[\lambda(\alpha_s / \alpha_l)^{1/2}]} \qquad (A2-1$$

Introducing the coefficients A and B into equations (A2-8) and (A2-9), we obtain the temperatures for the solid and liquid phases as;

$$\frac{T_s(x,t)-T_w}{T_m-T_w}=\frac{erf[x/2(\alpha_s t)^{1/2}}{erf(\lambda)} \qquad (A2-13)$$

$$\frac{T_l(x,t)-T_i}{T_m-T_i}=\frac{erfc[x/2(\alpha_l t)^{1/2}]}{erfc[\lambda(\alpha_s/\alpha_l)^{1/2}]} \qquad (A2-14)$$

The interface energy-balance equation (A2-7) is now used to determine the relation for the evaluation of the parameter λ. That is, when s(t), $T_s(x,t)$ and $T_l(x,t)$ from equations (A2-11), (A2-13) and (A2-14), respectively, are substitute into equation (A2-7), we obtain the following transcendental equation for the determination of λ;

$$\frac{e^{-\lambda^2}}{erf(\lambda)}+\frac{k_l}{k_s}\left(\frac{\alpha_s}{\alpha_l}\right)^{1/2}\frac{T_m-T_i}{T_m-T_w}\frac{e^{-\lambda^2(\alpha_s/\alpha_l)}}{erfc[\lambda(\alpha_s/\alpha_l)^{1/2}]}=\frac{\lambda L\sqrt{\pi}}{C_{ps}(T_m-T_w)} \qquad \text{(A2-15)}$$

Once λ is known from the solution of this equation, s(t) is determined from equation (A2-11), $T_s(x,t)$ from equation (A2-13) and $T_l(x,t)$ from equation (A2-14).

IMAGE EVALUATION
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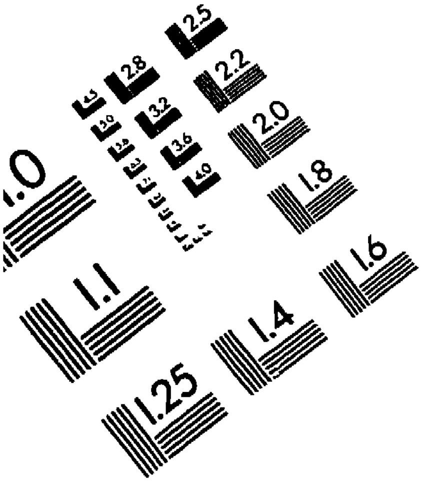
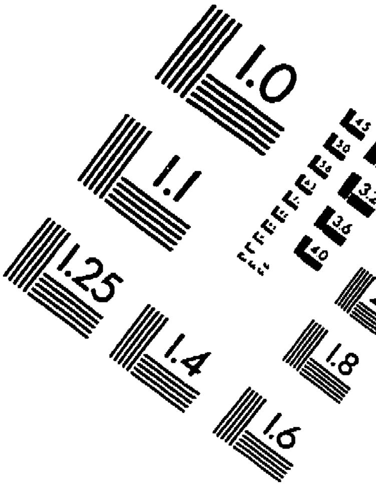
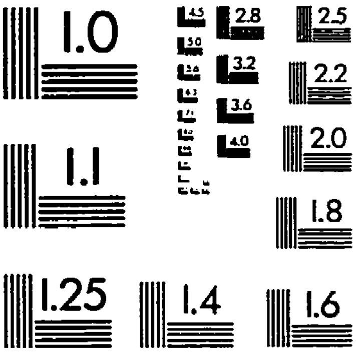

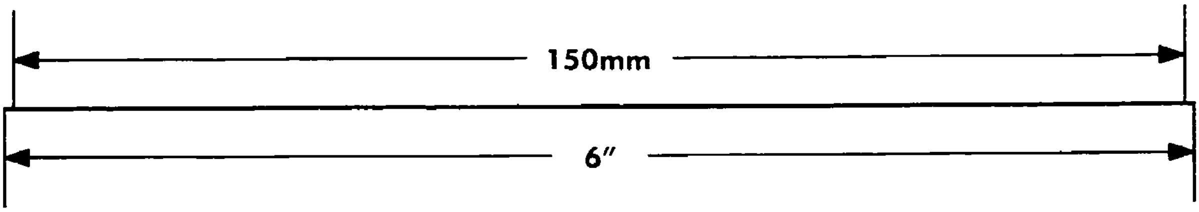

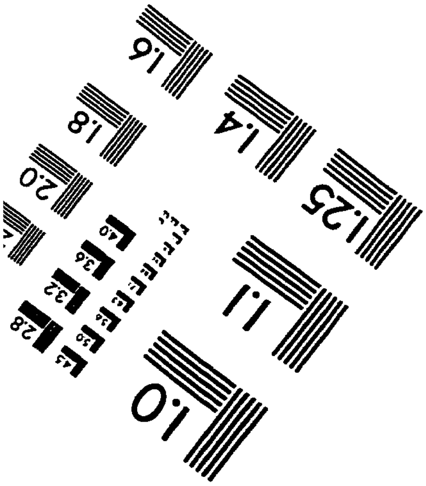
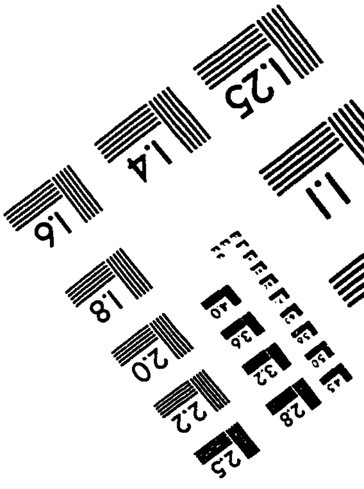

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