



Université catholique de Louvain

Faculté des Sciences Appliquées

Unité de Mécanique Appliquée
Unité de Chimie et de Physique des Hauts Polymères

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Crystallization of PolyEthylene Terephthalate in Injection Moulding :

Experiments, Modelling and Numerical Simulation

Dissertation présentée par
Olivier VERHOYEN
en vue de l'obtention du grade de
Docteur en Sciences Appliquées

Jury :

Professeur F. Dupret (UCL) : Promoteur
Professeur R. Legras (UCL) : Promoteur
Professeur P. Godard (UCL)
Professeur R. Keunings (UCL)
Professeur J.-M. Haudin (CEMEF - France)
Professeur H.E.H. Meijer (TUE - Hollande)
Professeur C. Trullemans (UCL) : Président

Février 1997

Accomplir cette recherche, des premiers projets à leur concrétisation, a été une expérience fructueuse et inoubliable. Fructueuse, par la collaboration entre le Laboratoire des Hauts Polymères et l'Unité de Mécanique Appliquée qui m'a donné l'occasion d'élargir mes horizons dans des domaines aussi variés que la simulation numérique et la physique des polymères. Inoubliable, par la chance d'avoir été entouré de personnes à la fois compétentes et sympathiques, toujours prêtes à m'épauler lorsqu'une difficulté surgissait. En ce sens, j'ai plaisir à exprimer mes plus vifs remerciements aux diverses personnes qui m'ont aidé à mener à bien ce travail.

Mes remerciements s'adressent tout d'abord aux Professeurs Roger Legras et François Dupret, promoteurs de ce travail, qui m'ont accueillis dans leur laboratoires respectifs et qui m'ont permis d'effectuer ce doctorat dans d'excellentes conditions. Leur rigueur scientifique et leurs critiques constructives ont continuellement enrichi mon travail. Pour vos encouragements et pour votre confiance, Merci.

Je remercie Monsieur Favier pour m'avoir ouvert les portes du Pôle Européen de Plasturgie (Oyonnax, France) et permis la réalisation des campagnes expérimentales d'injection. Plus particulièrement, je tiens à remercier vivement Jean-Pierre Gazonnet, Gérard Dechavanne et Virginie Durand pour leur accueil chaleureux et leur expertise en injection.

Ma reconnaissance va également aux membres du jury, les Professeurs Pierre Godard, Roland Keunings, Jean-Marc Haudin et Han Meijer qui ont accepté de passer du temps à lire et à évaluer ce travail ainsi que le Professeur Charles Trullemans qui en a accepté la présidence.

Je voudrais également remercier l'Institut pour la Recherche Scientifique dans l'Industrie et l'Agriculture (IRSIA) pour son soutien financier ainsi que le Docteur Pierre Decroly de la société Solvay et le Docteur Jean-Marc Dekoninck de la société Exxon Chemical pour leur soutien industriel.

Il m'est malheureusement impossible de remercier tous ceux qui, d'une manière ou d'une autre, m'ont aidé à réaliser ce travail. Aussi, je tiens à saluer l'ensemble des membres des unités POLY et MEMA pour le plaisir que j'ai eu à y travailler durant ces quelques années. Je me permets de citer Béatrice, Sophie, Aurore, Etienne, Jean-Jacques et

Victor pour leur assistance technique et logistique, Alain, Luc, Vincent pour m'avoir guidé dans le logiciel de simulation, Olivier pour avoir partagé le même bureau et débattu de nombreux sujets. Je remercie aussi Didier, Saïd, Catherine, Roger, Elisabetta, et tous ceux avec qui les discussions les plus diverses ont toujours été très instructives. Je remercie également Laurent avec qui j'ai initié ce travail ainsi que Philippe Dedonder et Ralph Jousten qui y ont participé.

Je n'oublie pas non plus tous les miens pour leur soutien et leurs encouragements constants et plus particulièrement Anne pour son aide et sa présence de tous les instants.

*Olivier Verhoyen
Enines (16 février 1997)*

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Summary

The aim of the thesis was to understand and to predict the flow and the crystallization of a thermoplastic polymer (PET) during the injection moulding process as a function of polymer properties and processing conditions. This pluridisciplinary objective has been reached by the combination of injection moulding and characterization experiments, mathematical modelling and numerical simulation.

From laboratory experiments (calorimetry and cone-plate rheometry), a new crystallization model, namely the *consecutive Avrami model*, has been developed. This model, which takes into account the effects of induction time, final degree of crystallinity and secondary crystallization, describes both isothermal and non-isothermal crystallization kinetics, including cold- and melt-crystallization. In order to correctly handle shear- and pressure- induced crystallization when complex shear and pressure histories are imposed to the polymer, it has been demonstrated that nucleation and crystal growth processes must be governed by distinct parameters, which was not the case in the first version of the *consecutive Avrami model*. Therefore an improved model has been proposed.

The principles of a general method for the numerical simulation of the injection moulding process has been described. In particular, a new numerical method has been developed in order to accurately take into account the effects of polymer rheology upon the flow and much attention has been paid to the calculation of the flow kinematics. In this field, it has been demonstrated that the gapwise velocity component cannot be neglected when dealing with semi-crystalline polymers. Two methods for predicting crystallinity have been investigated: a fully coupled method which is able to take effects of crystallization on viscosity, temperature and density into account, and a decoupled method based on the development of a

tracking algorithm able to reconstruct trajectories and thermo-mechanical histories of injected material particles.

Injection moulding experiments have been carried out to validate crystallinity predictions. PET plates, produced by means of an apparently simple mould however showed two unexpected behaviours. Successive flow fronts exhibited strange 'V' shapes at the cavity end while the gate was originally drawn to allow a linear filling of the cavity. Crystallinity distribution in the final parts exhibited an unexpected pattern with an intermediate region, showing little crystallinity, surrounding a highly crystalline core and being surrounded by the amorphous skin.

It has been observed that predicted pressure and temperature distribution as well as predicted heat flux at the wall were in agreements with experiments. It clearly appeared that pressure induced crystallization plays, after temperature, the major role upon the crystallinity development during the injection moulding of PET. Moreover, nuclei were mainly generated upstream of the runner system where the pressure reached highest values. On the other hand, shear-induced crystallization was found to be practically negligible.

Unexpected behaviours experimentally observed have been attributed to viscous dissipation in the runner system which generates a very important temperature rise in an annular region at the outlet of the runner. This temperature rise can be so important that it greatly affects both polymer flow and crystallization in the mould cavity through its impact on viscosity and on nucleation.

In this thesis, the crystallization model has been more often improved by simulating the injection moulding process than by performing laboratory experiments. Improving physical models by simulating complex experiments therefore appears as being very powerful, since the role of the different parameters of the model is complex and highly coupled.

Notation

Operators

$\bar{\nabla}$	$1/m$	gradient operator
$\bar{\nabla}_\alpha$	$1/m$	gradient operator with respect to the midplane
$\frac{D}{Dt}$	$1/s$	material derivative
$\mathbf{A}^d$	–	deviatoric part of a tensor
$\mathbf{A}^t$	–	transposition
$\text{tr}(\mathbf{A})$	–	trace

Subscripts and superscripts

n	time step number
h	discretized field
α	in-plane component
∞	equilibrium behaviour

List of principal symbols

c_p	$J/(kg\ K)$	heat capacity at constant pressure
e	J/kg	specific internal energy
$\tilde{f}$	N/kg	specific body forces
$f(\alpha_v^c)$	–	viscosity dependence of the relative crystallinity degree
h	m	local half-gap thickness

k	s^n	kinetic parameter (<i>Avrami model</i>)
k	$J/(Kms)$	heat conduction coefficient (energy equation)
k_B	J/K	Boltzmann constant
k_1	s^{n_1}	kinetic parameter (<i>consecutive Avrami model</i> , 1 st mechanism)
$k_1^*(\sigma)$	—	reduced kinetic parameter (shear stress dependent)
k_2	s^{n_2}	kinetic parameter (<i>consecutive Avrami model</i> , 2 nd mechanism)
l	—	pathline of a material point
$m_i(\cdot), \bar{m}_i(\cdot), m_i^*(\cdot)$		viscosity functions
n	—	Avrami coefficient (<i>Avrami model</i>)
n	—	power law index (<i>viscosity model</i>)
$\vec{n}$	—	unit outward vector
n_1	—	Avrami coefficient (<i>consecutive Avrami model</i> , 1 st mechanism)
n_2	—	Avrami coefficient (<i>consecutive Avrami model</i> , 2 nd mechanism)
p	Pa	pressure
$\vec{q}$	$J/(m^2 s)$	heat flux vector
r	$J/(kg s)$	specific heat source
t	s	time
t_n	s	discretized time
t_0^1	s	induction time (<i>consecutive Avrami model</i> , 1 st mechanism)
$t_0^{1*}(\sigma)$	—	reduced induction time (shear stress dependent)
t_0^2	s	induction time (<i>consecutive Avrami model</i> , 2 nd mechanism)
t_0^{i*}	s	induction time (non-isoth. cons. <i>Avrami model</i> , i^{th} mechanism)
u	m/s	velocity component along x -axis
v	m/s	velocity component along y -axis
$\vec{v}$	m/s	velocity vector
$\bar{v}_\alpha$	m/s	velocity parallel to the midplane averaged across the thickness
v_s	m^3	spherulite volume
w	m/s	transverse velocity component (along z -axis)
w^*	m/s	part of w velocity due to solidified thickness apparition
$\hat{w}$	m/s	part of w velocity due to change of thickness
w_1	—	weight fraction (<i>consecutive Avrami model</i> , 1 st mechanism)

$\vec{x}$	m	spatial position vector
$\vec{x}_s$	m	successive spatial position vector of a material point
x_α	m	in-plane co-ordinates
z	m	out-of-plane co-ordinates
D	$1/s$	rate of deformation tensor
G	m/s	growth rate of spherulite
G_e	J/kg	specific Gibbs energy
$F_n 0$	–	dependence of reduced shear stress upon reduced shear rate
H	J/kg	specific enthalpy
I	–	second order unity tensor
J_i	$m^{i+1}/(Pa\ s)$	terms in expression for fluidity S_o
L	m	characteristic length of the cavity
N	$\# / m^3$	number of nuclei
N_1	$\# / m^3$	number of fictive nuclei (<i>differential consecutive Avrami model</i> , 1 st mechanism)
$\dot{N}$	$\# / (m^3\ s)$	nucleation rate
P^h	Pa	discretized pressure field
Q_n	–	extrapolation mesh
R	J/K	ideal gas constant
R_1	m/m^3	total radius of N_1 (<i>diff. cons. Avrami model</i> , 1 st mechanism)
S	$J/(kg\ K)$	specific entropy
S_v	$m^3/(Pa\ s)$	fluidity in volume
S_ρ	$kg/(Pa\ s)$	fluidity in mass
S_1	m^2/m^3	total surface of N_1 (<i>diff. cons. Avrami model</i> , 1 st mechanism)
T	K	temperature
T_g	K	glass transition temperature
T^h	K	discretized temperature field
$\hat{T}_{n+1}^h$	K	provisional temperature field at time t_{n+1}
T_m	K	melting temperature
T_m^0	K	equilibrium melting temperature

$\dot{T}$	K/s	cooling rate
V^h	m/s	discretized velocity field
V_1	m^3/m^3	total surface of N_1 (<i>diff. cons. Avrami model, 1st mechanism</i>)
α	$1/K$	thermal expansion coefficient
α_f	—	fictive relative crystallinity degree
α_u	—	real degree of crystallinity
α_u^c	—	relative crystallinity degree
α_{u1}^c	—	relative crystallinity degree (<i>cons. Avrami model, 1st mechanism</i>)
α_{u2}^c	—	relative crystallinity degree (<i>cons. Avrami model, 2nd mechanism</i>)
α_u^∞	—	ultimate degree of crystallinity
$\alpha_u^{1,\infty}$	—	ultimate crystallinity (<i>consecutive Avrami model, 1st mechanism</i>)
$\alpha_u^{2,\infty}$	—	ultimate crystallinity (<i>consecutive Avrami model, 2nd mechanism</i>)
α_w^∞	—	ultimate degree of crystallinity (weight fraction)
χ	—	degree of crystallization
γ	—	crystallinity dependence of the specific mass
$\dot{\gamma}$	$1/s$	shear rate
$\dot{\gamma}_0$	$1/s$	characteristic shear rate of the fluid
η	$Pa\ s$	polymer viscosity
η_0	$Pa\ s$	reference viscosity (Newtonian viscosity in Cross law)
η_0^m	$Pa\ s$	reference melt viscosity
φ_i	—	linear shape functions
κ	$1/Pa$	isothermal compressibility coefficient
λ	$J/(Kms)$	heat conduction tensor
θ_i	—	cumulated induction time factor (<i>non-isoth. cons. Avrami model, ith mechanism</i>)
ρ	kg/m^3	specific mass
ρ_a	—	density of a 100% amorphous sample (room temperature)
ρ_c	—	density of a 100% crystalline sample (room temperature)
ρ_0^a	kg/m^3	specific mass of a 100% amorphous sample
ρ_0^c	kg/m^3	specific mass of a 100% crystalline sample

σ	Pa	shear stress
$\boldsymbol{\sigma}$	Pa	Cauchy stress tensor
τ	Pa	shear stress
$\boldsymbol{\tau}$	Pa	extra stress tensor
τ_0	Pa	characteristic stress of the fluid (Cross model)
ψ_i	—	quadratic shape functions
ω	$m/(Pa\ s)$	profile function
ΔH_m	J/kg	latent heat of fusion
ΔH_m^0	J/kg	equilibrium latent heat of fusion
Φ	—	volume fraction of sphere in a solvent
Γ_n, Γ_{n+1}		computation domain at time t_n, t_{n+1}
Γ_e	—	boundary at the gate
Γ_w	—	boundary at the lateral wall
$\Gamma_f(t)$	—	boundary at the progressing flow front
Γ^+	—	upper surface of the product
Γ_0	—	midsurface of the product
Γ^-	—	lower surface of the product
Γ^h	—	finite element mesh
$\partial\Gamma^h$	—	finite element mesh boundary
Λ_α	Pa/m	pressure gradient
Λ	Pa/m	norm of the pressure gradient

Chapter I

Introduction and literature survey

Abstract

One of the most important objectives of basic studies in polymer processing is to relate the properties and thermo-mechanical history of the polymer to the microstructure and ultimate properties of the plastic articles. In particular, the understanding and prediction of the crystallinity degree distribution, as developing during the injection moulding of semi-crystalline polymers, is of major interest owing to the important impact of crystallinity upon the resulting mechanical properties of the moulded parts. To introduce this thesis, the injection moulding process is shortly described to illustrate the complex thermomechanical history that material particles undergo during moulding, and the possible problems occurring during the process. The scientific and industrial relevance of the numerical simulation of injection moulding is pointed out. Basic concepts of polymer crystallization are summarized. The state of the art is described concerning the modelling and numerical simulation of the injection moulding process and the modelling of polymer crystallization kinetics. Finally, the objectives of this study are presented, together with the methodology that we have developed, and which combines experiments, mathematical modelling and numerical simulation.

1. Introduction

The last few decades have been accompanied by a rapid development of synthetic polymeric materials. Nowadays, and on a continuously increasing scale, polymers are used in many kinds of industrial products (e.g., in the aeronautic, automotive, container and toy industries). Compared to more traditional materials, polymers intrinsically exhibit a surprisingly wide combination of chemical, physical and electrical properties (such as low density, high specific strength and stiffness, high impact resistance, water impermeability, good optical properties and chemical inertness), that can be useful in a variety of applications. More important, in addition, is the ease and cheapness with which they can be processed. A single operation, with an automatic mass production equipment, can often be used to produce a ready to use article of considerable geometric complexity, with however high dimensional accuracy and surface finish.

It is well known that chemically identical polymeric parts can exhibit widely different mechanical properties as a result of differences in structure caused by the local mechanical deformation and thermal history experienced by the material during processing. A typical example is fibre spinning, where process induced molecular orientation and crystallization increase the stiffness of the spun material by an order of magnitude over that of the undrawn melt.

To manufacture articles with high specifications in terms of optical and mechanical properties or dimensional stability, an important knowledge is required, as illustrated in Fig. I.1, on how the processing variables, together with the mechanical and flow properties of the material and the geometry of the equipment, can influence the final properties of the product. Even when the qualitative relationship between morphology and product properties is firmly established, the quantitative prediction of morphology formation during processing and the prediction of product properties as a function of processing parameters is still lacking, resulting in the need of a large amount of trials and errors when new products are developed. This is especially true for complex manufacturing processes, such as injection

moulding, that combine large and fast mechanical deformations with high pressure and intense heat transfer.

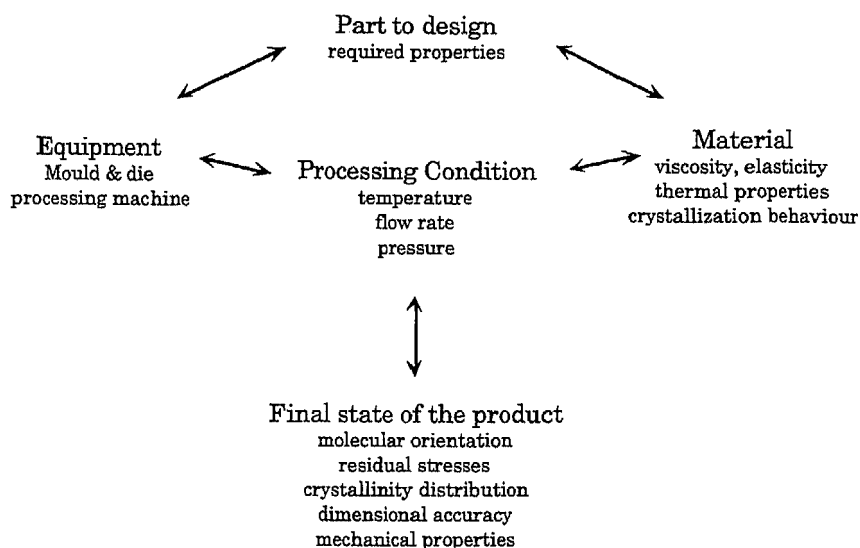


Figure I.1 : Interrelationships prevailing in polymer processing.

2. Injection moulding

Although a large number of industrial processes exists for the manufacturing of plastic products, about 30 % of the polymers are processed by injection moulding. The main reasons of this fact are the high production rates and the facility to combine several functions in one product, since parts that must be assembled when other production techniques are applied, can be formed into one single product when using injection moulding. Injection moulding of parts with complex shapes is thus becoming a widely used process for the mass production of plastic products.

2.1. The injection moulding cycle

A reciprocating screw injection moulding machine (Fig. I.2.) consists of two main parts, namely the injection unit and the clamping unit containing the mould. The function of the former is to melt the polymer and to inject it into the mould, whereas the latter automatically opens and closes the mould, and ejects the final

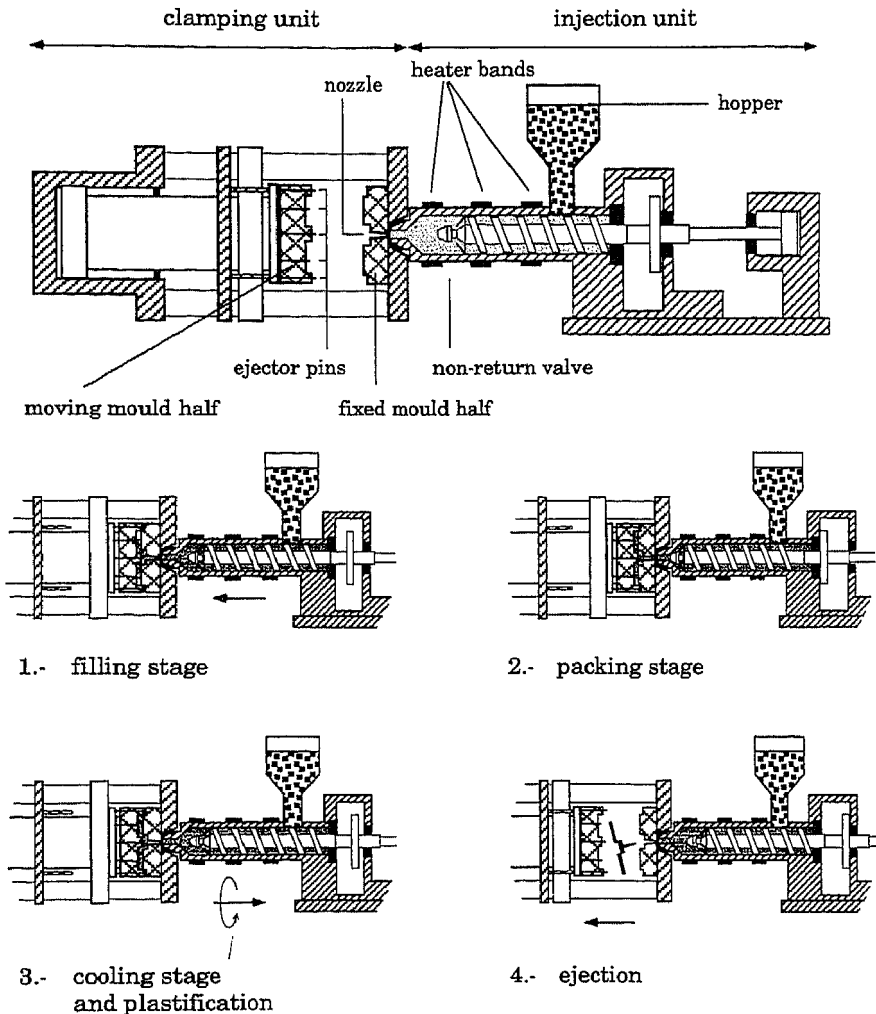


Figure I.2 : Schematic layout of a reciprocating screw injection moulding machine, and description of the main processing stages.

The following cycle takes place during the injection moulding of thermoplastic material (which is mostly supplied in a granular form) :

a – Plasticization stage. Granules of the moulding material are introduced via a hopper into an extruder, that consists of a screw rotating inside a heated barrel, where the material is transported towards the mould. The polymer is plasticized by the frictional heat generated by mechanical deformation and by heater bands which are fitted around the extruder cylinder. During transport, mixing homogenises the melt temperature. The plasticized polymer is accumulated in front of the screw, that is meanwhile moving backwards against the adjustable *back-pressure* (i.e. the hydraulic pressure exerted on the screw).

b – Filling stage. When enough material is accumulated, the screw is moved forward, by the hydraulic cylinder which acts as a plunger. The softened material is then injected at a high speed into the mould, through the nozzle, via the sprue that leads to the runner system. Backwards flow into the screw channel is prevented by a non-return valve. The driving pressure or velocity of the screw is, in most cases, controlled by a microprocessor system.

c – Packing stage. After mould filling, and in order to prevent further shrinkage of the part due to cooling and solidification, the material is maintained under a high pressure that forces more material to enter the cavity. Without this extra flow, the volume shrinkage that is of about 10 % for an amorphous thermoplastic and of about 20 % for a semi-crystalline thermoplastic, would generate shrinkage cavities, leading to bad properties and an unacceptable appearance of the product.

d – Cooling stage. When the gate seals, no more material can enter the cavity and the product cools without compensation for shrinkage. In the meantime, the extruder plasticizes a new batch of material in order to restart the cycle.

e – Ejection. When the material has acquired enough stiffness, the clamping unit opens the mould and the part is ejected, usually by means of ejector pins.

2.2. Problems occurring in the injection moulding process

As injection moulding is a complex process, defaults that affect the product quality can appear when starting the design of a new mould, when changing from a well-known to a new material, or even during the regular operation of a mould. Because of the interdependence between the various processing conditions, there are often many causes for defects during moulding. In addition, many of the possible problems can be worsened by a bad mould design. The most frequent problems are listed below.

- Short shots are usually caused by the material solidifying before it completely fills the cavity. Possible causes are insufficient pressure, too short injection time, a cold mould, or an unbalanced runner system in a multi-cavity mould, ...
- Part flashing is usually caused by a mould deficiency. Other causes can be the injection force being higher than the clamping force, an excess of fluidity due to overheated material, insufficient venting, excess feed, ...
- Sink marks or voids are usually caused by insufficient pressure exerted on the parts, insufficient material packed into the cavity, too hot material when the gates freeze, ...
- Poor weld lines are caused by insufficient temperature and pressure at the weld location, or a bad feeding system design.
- Brittleness and discoloration are caused by degradation of the material during moulding.
- Excessive shrinkage occurs when insufficient material is injected into the mould, which is usually caused by a wrong design of the cavity, especially concerning the location of the gates, and/or a bad selection of moulding conditions.
- Warpage occurs when the shrinkage is different along the part. This may be caused by non-homogeneous cooling or by frozen-in molecular orientation leading to non-homogeneous residual stresses.
- Overpacking occurs when too much material is forced into the mould, which reduces the normal shrinkage and results in difficulties to eject the product from the mould.

2.3. Relevance of numerical simulation

Despite the fact that constant processing parameters, as well as homogeneous material properties are essential prerequisites for high quality production, it is predominantly the mould design that governs the quality of injection moulded parts. For example, the location of the cooling channels has an important effect on the cycle duration, on the temperature of the cavity surface, and consequently on the thermally induced stresses and warpage.

Because it is usually impossible to compensate for deficiencies in the mould design by adjusting the processing parameters during production, expensive mould corrections are often necessary. In order to prevent these imperfections and to reduce the time spent in the design of new moulds, designers are more and more using injection moulding simulation programs. Indeed, numerical simulation provides tools that can speed up product innovation and reduce the costs involved by empirical attempts. Most of the currently available simulation software are able to predict the filling time, the progression of the melt front, the occurrence of short shots, the location of weld lines and air traps, and the final distributions of pressure and temperature in the part. These programs have proven to be of high value in the design of the moulds and the delivery channels, giving the opportunity to optimise the location of gates and air vents and to evaluate the necessary clamping force, the machine size and the overall cycle time. Usually, this is where simulation ends, for most mould designers.

Nowadays however, injection moulding is more and more applied to products that require high dimensional and optical accuracy (such as compact discs, optical lenses, glass fibre connectors, micromechanical elements, ...). In these cases, the prediction of the product properties as a function of the tool design, the processing conditions and the chosen material must be included in the model, leading to an integral approach of the simulation of injection moulding. The new generation of software must therefore deal with all the three process stages (filling, packing and cooling) and must accurately represent all the important effects like fountain flow, viscous dissipation, molecular orientation, frozen stresses, microstructure, crystallization, etc., together with their impact on the process and the product.

The flow of a polymer melt into a cold cavity is a typical example of an unsteady, non-isothermal, three-dimensional flow of a compressible viscoelastic fluid. During the whole process, the polymer (which passes from a fluid to a rubbery, glassy or semi-crystalline state) is subject to mechanical and thermal influences that affect the properties of the injection-moulded parts. For semi-crystalline polymers, in particular, the interaction between the molten polymer and the thermal and mechanical conditions that exist in the mould cavity during the filling, packing and cooling stages can strongly influence the development of microstructures in the moulded part which, in turn, will significantly affect the end-use properties of the moulded articles (e.g., physical and mechanical properties, dimensional stability, appearance, ...).

3. Polymer crystallization

3.1. Basic thermodynamic concepts

Crystallization is a phase transformation process which is caused by a change in the thermodynamic state of the system, for example by lowering its temperature below a critical value, or by increasing its hydrostatic pressure. When a liquid polymer is supercooled to a temperature below its melting temperature, small polymer crystals appear at random in the liquid and start growing. The driving force of crystallization is mainly internal, and is generated by the excess of thermodynamic free energy in the system. In the case of polymers, the crystallization process is kinetically controlled, the motion referring to the transport of molecules from the disordered liquid phase to the ordered solid phase, and to the rotation and rearrangement of the molecules at the surface of the crystal.

The specific Gibbs free energy G_e of any system is given by the expression :

$$G_e = H - T S \quad , \quad (1)$$

where H and S are the specific enthalpy and entropy, respectively, and T is absolute temperature. In the case of a crystallization taking place without any volume constraint, the change in Gibbs free energy is given by the relation :

$$\Delta G_e = (H_{crystal} - H_{melt}) - T(S_{crystal} - S_{melt}) = \Delta H - T \Delta S \quad . \quad (2)$$

To a first approximation, the change in enthalpy, ΔH , is equal to the latent heat of fusion, and ΔS is equal to the entropy of the melt (the entropy of the crystal being much smaller by comparison). By definition, at the equilibrium melting temperature, T_m^0 , the change in free energy vanishes :

$$\Delta H = T_m^0 \Delta S \quad . \quad (3)$$

Below that temperature the system will spontaneously seek to minimise its free energy by crystallizing, which involves two independent phenomena : nucleation and growth.

3.2. Nucleation

Two physical mechanisms are possible for the *primary nucleation* of bulk crystallized polymers, namely *homogeneous nucleation*, which (rarely) occurs in a homogeneous supercooled melt, and *heterogeneous nucleation*, which occurs at the surface of foreign bodies. Heterogeneous nucleation always occurs with a lower supercooling than homogeneous nucleation. The surface heterogeneities involved in the nucleation process are frequently referred to as the *nucleating agents*.

In the absence of existing solid particles, fluctuations occur in the melt which lead to the formation of small crystalline entities. The replacement of the old phase by the new one is accompanied by a decrease of the Gibbs free energy, whereas the formation of an interface between the two phases causes this free energy to increase. Above the equilibrium melting temperature, the value of ΔG_e , as defined in Eq. (2), monotonically increases with an increasing size of the entity. Below the equilibrium melting temperature, this function changes to a function, which is represented in Fig. I.3, which has a maximum, defined by :

$$\frac{d\Delta G_e}{dr} = 0 \quad , \quad (4)$$

where r is the radius of the entity. This maximum, noted as ΔG_e^* , can be regarded as being the activation energy barrier, that corresponds to a critical size of the entities. For smaller entities, called *embryos*, the decrease of bulk free energy is exceeded by the increase in interfacial free energy. Embryos therefore tend to re-dissolve. In order that an entity be stable, it must spontaneously grow to the critical size with an associated critical free energy ΔG_e^* . Such entities, which will further tend to grow, are called *nuclei*. When the critical equilibrium nucleus size is not immediately reached in the supercooled state, the new phase can only appear after an incubation period which is called the *induction time*.

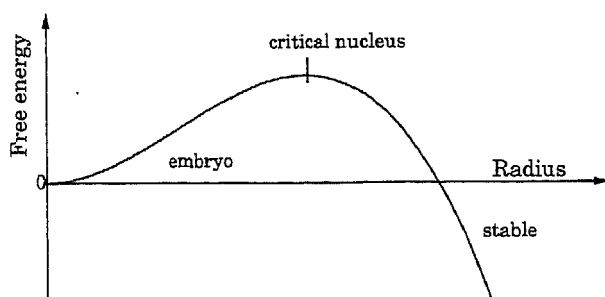


Figure I.3 : Schematic representation of the change in free energy as a function of size illustrating the nucleation process.

The rate of nucleation is calculated by using the Boltzmann law together with kinetic considerations¹. Because entities with a free energy exceeding ΔG_e^* can grow into nuclei, the rate of nucleation per unit volume $\dot{N}$ is written in the form :

$$\dot{N} = \dot{N}_0 \exp(-\Delta E/k_B T) \exp(-\Delta G_e^*/k_B T) \quad , \quad (5)$$

where $\dot{N}_0$ is a constant, k_B is the Boltzmann constant and the term $\exp(-\Delta E/k_B T)$ is the probability for a chain segment to be transported from the supercooled to the crystalline phase, ΔE being the activation free energy of the process. The temperature dependence of this activation energy has been determined by Hoffman and Lauritzen² by using the empirical viscosity relation of Williams, Landel and Ferry (which, properly speaking, can only be applied between T_g and T_g+100). It

must be pointed out that ΔG_e^* is also temperature-dependent, while an expression has been given by Van Antwerpen³. All this leads to the following expression :

$$\dot{N} = \dot{N}_0 \exp\left(-\frac{C_1}{R(C_2 + T - T_g)}\right) \exp\left(-\frac{f() (T_m^0)^4}{k_B \Delta H_m^2 T^3 \Delta T^2}\right), \quad (6)$$

where T_g is the glass transition temperature, C_1 and C_2 are material constants, R is the ideal gas constant, ΔH_m is the latent heat of fusion, $f()$ is a function related to the surface energies of the nuclei, and $\Delta T = T_m^0 - T$.

A general discussion of heterogeneous nucleation has been given by Binsbergen⁴ leading to a different expression for ΔG_e^* :

$$\Delta G_e^* = \frac{f() (T_m^0)^2}{(\Delta H_m \Delta T \rho_c)^2}, \quad (7)$$

where ρ_c is the crystal density.

Nucleation processes are very important in polymer crystallization because they dominate not only the initial formation of the crystalline entities, but also their subsequent growth.

3.3. Growth

In quiescent crystallization processes, the general nucleation and growth response of polymeric materials consists in developing a superstructural morphology which is predominantly spherulitic. Fig. I.4 shows a simplified sketch of the general spherulitic structure of polymer crystals from a microscopic point of view. The spherulites can be regarded as a more or less organised arrangements of crystallites embedded in an amorphous mass. Therefore, a crystallized polymer is in reality semi-crystalline, while the maximum degree of crystallinity can reach between 20 and 80 %, depending on the type of polymer and the crystallization conditions. Crystallites can be considered as being highly ordered regions, with parallel molecular chains which are mostly folded back and forth, as it can be seen in the close-up of Fig. I.4.

The growth of the crystals depends on the rate of molecular deposition on the lateral surfaces of the nucleus. No growth occurs in the chain direction, because the folds interrupt the crystal lattice and block (by their fixation in the crystal) any

simple mechanism of thickness increase. On the crystal surface, a new layer can therefore only be grown after *secondary* or *tertiary nucleation*. The former applies to the deposition of the first straight section onto a smooth flat surface, which acts as a nucleus of secondary order starting a new layer of chains. The latter refers to the addition of such sections on the outer ledges of the secondary nucleus up to the completion of this layer. These processes are basically similar to primary nucleation, but with a somewhat lower free enthalpy barrier since the newly created surface area is smaller.

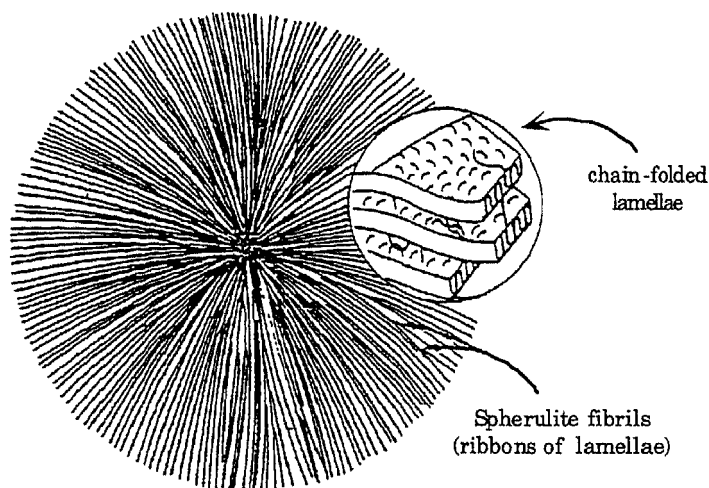


Figure I.4 : Schematic representation of the general spherulitic structure.

With regard to the growth of spherulites, the basic assumption is made that the growth rate is limited by the frequency of the formation of successive monolayers. Analogous to Eq. (5), Hoffman and Lauritzen² derived an equation for the rate of secondary nucleation :

$$\dot{I} = \dot{I}_0 \exp(-\Delta E/k_B T) \exp(-\Delta G_2^*/k_B T) \quad , \quad (8)$$

where $\dot{I}$ is the rate of nucleation per unit surface and $\dot{I}_0$ is a frequency factor.

Since the growth rate is determined by the formation rate of nuclei on the substrate, Eq. (8) may be modified to represent the spherulite growth rate G . One obtains the expression :

$$G = G_0 \exp(-\Delta E/k_B T) \exp(-\Delta G_2^*/k_B T) \quad , \quad (9)$$

with G_0 being a constant.

3.4. Overall crystallization

At the macroscopic level, crystallization is usually described by a general kinetic equation of the following form :

$$\chi(t) = \int_{\tau=0}^t [T(\tau), \sigma(\tau), p(\tau)] \quad , \quad (10)$$

where χ is a measure of the extent or degree of crystallization, t is the time elapsed from the onset of crystallization, and $T(\tau)$, $\sigma(\tau)$, $p(\tau)$, are the temperature, shear stress and pressure histories. The fraction χ is defined as the time dependent ratio between the crystalline volume and the final crystalline volume. It goes from 0, before crystallization starts, to 1 at the end of the process.

It is necessary to distinguish between the above defined degree of crystallization and the degree of crystallinity (α_v), which is the most interesting quantity :

$$\alpha_v(t) = \frac{\text{crystallized volume (function of time)}}{\text{total volume}} \quad .$$

In general, the specific volume of polymers depends on the temperature, shear and pressure histories, and can change along the spherulite radius. Other quantities are also defined : the ultimate degree of crystallinity α_v^∞ :

$$\alpha_v^\infty = \frac{\text{total crystallizable volume}}{\text{total volume}} \quad ,$$

and the relative crystallinity α_v^c :

$$\alpha_v^c(t) = \frac{\text{crystallized volume (function of time)}}{\text{total crystallizable volume}} \quad .$$

The ultimate degree of crystallinity strongly depends on crystallization conditions. The degree of crystallinity α_v may not have a one-to-one correspondence with the degree of crystallization χ while it is related to α_v^∞ and α_v^c by the relation :

$$\alpha_v(t) = \alpha_v^\infty \alpha_v^c(t) \quad . \quad (11)$$

The macroscopic description of the crystallization kinetics deals with the geometrical and spatial aspects of the growth process. It aims, in order to quantify the transformation, to obtain a model for the general equation (10). The knowledge of the linear growth rate and the primary nucleation rate should, in principle, be sufficient to calculate the overall crystallization rate.

3.5. Influence of a shear flow on crystallization

It has been observed that the crystallization kinetics and the resultant polymer morphology can be altered when the melt is sheared⁵ or when polymer films or networks are stretched⁶⁻⁸. The crystallization time may be of several orders of magnitude lower for a sheared melt than that required under quiescent conditions. This was observed for a wide variety of polymers (PE⁹⁻¹¹, PB-1^{12,13}, PEO^{14,15}, PP¹⁰, ...).

Kobayashi and Nagasawa⁹ have studied the shear-induced crystallization of high and low molecular mass PE. They observed that the rate of crystallization, and especially the nucleation rate, rapidly increases with shear rate, while the induction time is decreasing. Increasing the shear rate in a high molecular weight material produced a more pronounced reduction of the induction time. They also observed that the superstructures of a specimen crystallized from a sheared melt can be quite different from that of a specimen crystallized without shear.

Lagasse and Maxwell¹⁰, while studying the shear-induced crystallization of PE and PP in a parallel plate rheometer, have found that shear has a strong accelerating effect on crystallization when the deformation rate exceeds a critical value. Moreover, the resulting crystal morphologies differ above and below this critical shear rate. At shear rates above the critical value, a fine fibrillar-like morphology, oriented in the flow direction, was observed. In contrast, below this critical value, the plateau region of induction times was characterized by unoriented spherulite structures, with exactly the same morphology as resulting from the crystallization of a quiescent, unsheared melt. They also observed that a higher molecular mass material crystallizes faster at a given shear rate and temperature.

Finally, shear-induced crystallization of PP was shown to be unaffected by the presence of either a carbon black additive or a heterogeneous nucleating agent.

Wolkowicz¹³ has studied the nucleation and growth behaviour of a PB-1 melt as a function of undercooling and shear rate. He observed two important features, namely an increase of crystallinity with shearing, which can mainly be related to a multiplication of the number of nuclei (and not by a significant change of the growth speed), and an increase of the shear stress, corresponding to a massive crystallization that happened some time only after the establishment of the steady flow.

Two molecular models have been proposed to explain the capability of simple shear to accelerate crystallization from the melt. The first model considers that entanglements between molecules in a steady flow act as temporary crosslinks and thereby cause an elastic extension of the chain segments¹⁶. This chain orientation facilitates the nucleation process, which effectively produces more crosslinks, leading to accelerated crystallization. The entanglements in the melt are transient in nature, and are affected by temperature and shear. Secondly, it has been suggested that heterogeneous particles in the sheared melt can generate localized flow disturbances that stretch the molecules and thereby enhance nucleation¹². Lagasse and Maxwell¹⁰ have investigated these two models and concluded from their experiments that the hydrodynamic origin of shear-induced crystallization can be attributed to the elastic chain extensions that are due to entanglement couplings between the molecules. Furthermore, they have suggested that transient orientation effects during the start-up of shear flow may have a dominant influence on the observed phenomena. Ulrich and Price¹⁷ have found a strong dependence of the nucleation rate of PEO upon supercooling and imposed stress. Since their work was carried out at low shear, in the Newtonian region, it seems that the observed effects result from the orientation of the molecular chains through the elastic nature of the melt rather than through flow orientation. This elastic orientation should lead to an additional supercooling of the system. This conclusion is in agreement with the results of Kobayashi and Nagasawa⁹, who exhibited an acceleration of crystallization for molecular mass materials substantially below the critical entanglement value.

4. Objective of the thesis

The objective of the research reported in this thesis is to understand and predict the crystallinity degree distribution that is formed during the injection moulding process, with a view to developing and implementing a validated computational method for the process simulation. This includes the goal of predicting the crystallinity degree distribution as a function of polymer properties and processing conditions. The work focuses in particular on the development of an accurate model for the crystallization behaviour of polyethylene terephthalate (PET).

This pluridisciplinary objective has been reached by the combination of experiments, mathematical modelling and numerical simulation. The scheme of the work (which has consisted of three steps) is summarized in Fig. I.5.

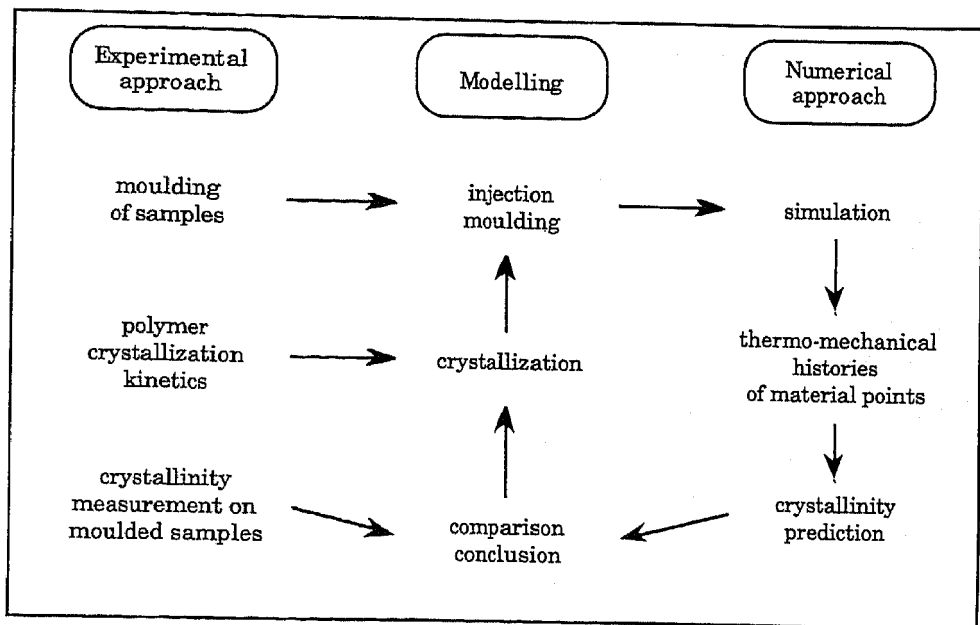


Figure I.5 : Scheme of the thesis.

From accurate experiments, adequate mathematical models for the injection moulding process and for polymer crystallization have been developed (step 1).

Numerical methods have subsequently been introduced to analyse the crystallization models and to develop a numerical simulation software for injection moulding (step 2). The validation of predicted crystallinity results by a comparison with experimental data has shown to be of great importance, leading to the improvement of both crystallization and injection moulding models (step 3).

5. State of the art

Many researchers have focused their attention on modelling the injection moulding process while others have concentrated their works on modelling polymer crystallization. This section deals with aspects that have already been investigated in these fields.

5.1. Crystallization kinetics modelling

Although numerous investigations have been reported about the kinetics of isothermal crystallization in polymers, only a few publications deal with the quantitative evaluation of the non-isothermal crystallization process or with shear-induced crystallization.

The first effort to quantitatively describe macroscopic development of crystallinity in terms of nucleation and linear crystal growth has been made by Kolmogoroff¹⁸, Avrami¹⁹ and Evans²⁰. Avrami considered the kinetics of phase change by ignoring the fact that the volume of untransformed material is constantly decreasing. His treatment introduces the concept of *phantom* or *fictitious nuclei* within the already transformed phase. Mathematically, this is a shortcut since it allows to conveniently determine the amount of phase transformation while the effects of impingement are taken into account by subtracting from the total the fictitious nuclei which develop and grow. Evans, on the other hand, has proposed a formulation of phase transformation by using the Poisson solution to a problem associated with the random fall of raindrops in a pond, which is analogous to the problem of nucleation and growth of two-dimensional spherulites in a thin layer of

melt. Although different approaches have been used, the contribution of these two authors has been demonstrated to provide similar models²¹. Only the approach of Avrami will therefore be summarized.

Under the assumption that quiescent isotropic spherulites are formed, the volume at time t of a spherulite nucleated at position $\vec{x}$ and time τ , is :

$$v_s(\vec{x}, t, \tau) = \frac{4}{3}\pi \left(\int_{\tau}^t G(\vec{x}, s) ds \right)^3 . \quad (12)$$

The fictive crystalline volume fraction α_f is expressed as the sum of the contributions, at time t , of all the crystals that have appeared in the time interval $[0, t]$:

$$\alpha_f(\vec{x}, t) = \int_0^t \dot{N}(\vec{x}, \tau) v_s(\vec{x}, t, \tau) d\tau , \quad (13)$$

where $\dot{N}(\vec{x}, \tau)$ is the nucleation rate per unit volume, including the fictitious nuclei that have appeared into the previously crystallized fraction. Under quiescent crystallization conditions and for a particular nucleation mechanism, Eq. (13) reduces to :

$$\alpha_f(\vec{x}, t) = k(\vec{x}, t) t^n , \quad (14)$$

where k is defined as the kinetic parameter and n is the Avrami coefficient. In order to determine the effective crystallinity distribution (α_v^c) from the fictive crystalline fraction (α_f), the following equation is used :

$$\frac{D \alpha_v^c}{D t} = (1 - \alpha_v^c) \frac{D \alpha_f}{D t} , \quad (15)$$

which is known as the Avrami postulate. Combination of Eqs. (14) and (15) leads to the well-known simplified Kolmogoroff-Avrami-Evans equation :

$$\alpha_v^c = 1 - \exp(-k t^n) . \quad (16)$$

Hillier²² and Price²³ have extended the Avrami model in order to account for the secondary crystallization occurring within existing spherulites, while Velisaris and Seferis²⁴ have considered primary and secondary crystallization as parallel and independent mechanisms.

It is usually assumed that the crystallization process obeys the principle of additivity. This principle is based on the assumption, (the so-called *isokinetic assumption*), that the instantaneous rate of transformation is a function of temperature and transformed fraction only, while it does not depend on the thermal history of the transformation. It follows that the transformation rate can be written in the form :

$$\frac{D\alpha_v^c}{Dt} = f_1(T, \sigma, p) f_2(\alpha_v^c) \quad , \quad (17)$$

where f_1 is a function of temperature, shear stress (or shear rate) and pressure, and f_2 is a function of the amount transformed.

Ziabicki²⁵, Ozawa²⁶ and Nakamura *et al.*²⁷ have derived kinetic equations based on the Avrami theory of phase change. The Ziabicki theory²⁵ is based on the assumption that non-isothermal crystallization can be treated as a sequence of isothermal crystallization steps and that polymer crystallization can be represented by a first-order kinetics. Ozawa²⁶ has developed a simple method for determining the Avrami exponents from non-isothermal differential scanning calorimetry (DSC) experiments, assuming that crystallization takes place at a constant cooling rate and originates from a distribution of nuclei that grow as spherulites with a constant radial growth. This model has been extended by Billon²⁸ to account for non-constant cooling rates. Nakamura *et al.*²⁷ have extended the Avrami equation to non-isothermal crystallization, by means of isothermal crystallization data. In these three approaches, secondary crystallization is considered as negligible. Patel and Spruiell²⁹ have demonstrated that an overprediction of non-isothermal data can be attributed to the fact that traditional kinetic models do not account for induction time.

Janeschitz-Kriegl and co-workers³⁰⁻³³, and Tribout³⁴ have independently developed theoretical models of shear induced crystallization by combining elements of polymer melt rheology and crystallization physics. All the features that can be expected for this process are (at least qualitatively) exhibited by these models. In particular, they show under which circumstances the simple concept of a constant critical deformation rate, as introduced by Lagasse and Maxwell¹⁰, can be useful.

Before these contributions, no theory of shear-induced crystallization was available offering the possibility for kinetic parameters to be determined from independent experiments; the effect of shear was introduced into quiescent crystallization kinetic models, in a purely empirical manner³⁵⁻³⁸.

5.2. Process simulation

The simulation of the injection moulding process for molten polymers has received considerable attention in literature. First research was largely devoted to predicting the moulding pressure (needed for equipment sizing) and the filling pattern (needed for mould design, gating and venting). Today, the tendency is to predict the final properties of injection moulded products, as a function of processing conditions, rather than to solely analyse the product mouldability.

At first, a 1½D approach was developed³⁹⁻⁴³ for the filling stage, since only the uni-directional flow between two parallel plates separated by a narrow gap was considered. The temperature field was however two-dimensional and assumed to depend on the flow and gapwise coordinates. Geometries were rectangular, circular or tubular. A generalized Newtonian fluid behaviour was adopted, where the temperature dependence of viscosity was assumed to be responsible for the coupling of the balance equations. Equations were solved by means of analytical or finite difference techniques.

The simulation of the filling of more realistic and complex geometries turned out to be the next step. A general 2½D approach was first introduced by Hieber and Shen⁴⁴ and Hieber *et al.*⁴⁵, who combined a finite element method for solving the 2D pressure field with a finite difference method for solving the 3D temperature and velocity fields. The finite element method is able to handle geometries of arbitrary shape. The finite difference scheme can accurately represent large gradients in the thickness direction, without the need of an excessive computing time. However, with this approach, some problems are found in the description of the flow front motion, while instabilities can develop and long calculation times are needed. Nevertheless, this approach was later improved and/or extended by many other authors. The determination of the flow front position represents in fact a key issue in the

simulation of the filling stage of injection moulding and several methods have been proposed. The flow analysis network (FAN)^{46,47} or volume-of-fluid (VOF) technique for front tracking can be used to form a control-volume scheme which handles automatic melt-front advancement in practical three-dimensional thin geometries. Alternative methods are the use of a numerically generated finite difference grid of complex shape⁴⁸, or the generation of successive finite element meshes covering the filled part of the cavity as developed by Dupret and his group⁴⁹⁻⁵⁴, who also demonstrated that an appropriate model of fountain flow must be introduced in order to take into account the important heat advection which is present in the gapwise direction in the front region⁵⁰.

The analysis of the transient flow and temperature fields during the post-filling stages of the process requires to account for the compressibility of the polymer material. Greener⁵⁵ has investigated (with major simplifying assumptions) the influence of the pressure and temperature history upon the density distribution in an injection moulded sample. Kamal and Kenig^{56,57} have extended the 1½D approach to the packing stage of the process. More recently, Kamal and Lafleur^{58,59} and Nguyen and Kamal⁶⁰ have analysed the entire injection moulding cycle, taking a viscoelastic material behaviour into account. Kabanemi⁶¹ has introduced polymer compressibility in the 2½D approach, which was also extended to packing stage analysis. A concise 2½D analysis of the whole injection moulding cycle was recently performed by Chiang *et al.*⁶²

Nearly all currently available software (*C-MOLD*, *MOLDFLOW*, *INJECT-3*, *MOLDSYS*, ...) use the 2½D approach for all the process stages, combined with a generalized Newtonian fluid behaviour during filling and/or differential or integral viscoelastic models to account for viscoelastic stresses in a direct or decoupled approach. Several product properties can be predicted for amorphous thermoplastics. Among them are the flow-induced stresses⁶³⁻⁶⁷, the residual stresses⁶⁴⁻⁷³ (which include both thermally-induced and pressure-induced stresses), the density distribution^{74,75}, and the dimensions and shape of the final part, including the prediction of shrinkage and warpage.^{61,76-78}

However, no much attention has been paid in literature to apply an accurate polymer crystallization model to the numerical simulation of injection moulding. Kamal and Lafleur⁷⁹ have studied heat transfer in the injection moulding of HDPE by using the Nakamura crystallization model. Dufossé⁸⁰ and Tribout³⁴ have studied PE and PP crystallization respectively by means of an extension of the Ozawa model in which thermal and shear effects were empirically introduced. They have compared with experiments the predicted development of the solidified layer during the process. Hsiung and Cakmak⁸³ have analysed the effects of mould temperature, flow rate and holding time on the crystallinity distributions of PEEK by means of a Nakamura model in which the effects of temperature and shear were also empirically introduced. More recently, Isayev *et al.*⁸¹ have studied the crystallization of PP by means of the Nakamura model, by introducing shear effects thanks to the model developed by Janeschitz-Kriegl and co-workers. The influence of the melt and mould temperature, the injection speed and the packing time was studied and predictions were compared to experiments. All these works have combined more or less sophisticated crystallization model with a 1½D approach.

6. Outline of the thesis

The chapter II of this thesis concerns the experimental study of isothermal and non-isothermal crystallization of PET, from which a suitable crystallization model is developed – including all the major effects present in polymer crystallization (namely, induction time, both primary and secondary crystallization mechanisms and ultimate degree of crystallinity).

Chapter III is devoted to analyse the effects of shear on the crystallization of PET. The model developed in Chapter II is extended to account for complex shear histories as encountered in the injection moulding process.

A complete mathematical model of injection moulding is described in Chapter IV. The resulting partial differential equations cannot be solved analytically, since they are non-linear, coupled and defined on a complex and

changing domain. A finite element model to obtain approximate solutions of these equations is therefore presented. Two methods for the prediction of crystallinity are also proposed, namely a fully coupled method and a decoupled method (which is based on the development of a tracking algorithm in order to reconstruct the trajectories and thermo-mechanical histories of injected material points).

Before to validate crystallinity predictions in moulded parts, deeper analyses of the influence of rheology on the polymer flow and of the tracking algorithm accuracy have been carried out by simulating the filling stage of amorphous polymers in several cavities.

As most polymers (and in particular PET) have a rheological behaviour which is governed by the Cross viscosity law, an appropriate numerical method is developed in Chapter V to easily introduce this behaviour in the simulation software. Numerical simulations of the filling of several cavities by means of polycarbonate are presented in order to highlight the effect of rheology on the flow and the pressure distribution in the cavity.

Chapter VI deals with a simple example that demonstrates the major effect of the transverse velocity component, which is often neglected in the case of thin parts, on the thermomechanical history of injected particles. In this chapter, an example taken from literature which deals with the filling of a rectangular plate by polystyrene is re-examined in order to compare numerical results obtained when this velocity component is neglected or not.

In Chapter VII, the crystallization model developed in Chapters II and III is used together with the injection moulding model described in Chapter IV in order to predict crystallinity distribution in a moulded part. Numerical predictions are compared to experiments in order to validate the approach and to draw conclusions.

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Chapter II

Isothermal and Non-isothermal Crystallization Kinetics of PET : Mathematical Modelling and Experimental Measurement

Abstract

Results obtained by differential scanning calorimetry have been used to develop a macro-kinetic model for the crystallization behaviour of semi-crystalline polymeric materials. Our model, which takes into account the effects of induction time, final degree of crystallinity and secondary crystallization, describes both isothermal and non-isothermal crystallization kinetics, including cold- and melt-crystallization. Experimental data obtained with polyethylene terephthalate (PET) in a wide range of thermal conditions compare well with predictions.

1. Introduction

The present work has been undertaken in order to introduce crystallization phenomena in the injection moulding simulation software developed by Dupret and his group^{1,7}. A large variety of models can be used to describe the crystallization kinetics of polymers. In the framework of process modelling, Patel and Spruiell⁸ recently presented a review of some of these models, including the most widely used Nakamura equation⁹. These authors pointed out that all models currently available are inadequate in predicting non-isothermal crystallization kinetics on the basis of isothermal data. They also went out to suggest using non-linear regression to directly fit the Nakamura equation to non-isothermal crystallinity data.

Studies of the crystallization kinetics of PET have shown three well known physical phenomena. First of all, an induction time is observed, which widely depends on temperature. Secondly, the ultimate degree of crystallinity in a sample can easily vary from the amorphous state up to 60% of crystallinity, depending on the crystallization conditions. Finally, a non-negligible secondary crystallization is also present. In order to take these phenomena into account, we will first review the available isothermal crystallization models, from which a more convenient approach will be developed for PET. A method to model non-isothermal crystallization on the basis of isothermal data will be developed in a second stage, and the experimental measurements and computational procedures needed to obtain the parameters of the new model will be investigated. Finally, some results will be presented and discussed. The effects of shear and pressure will be analysed in Chapters III and VII.

2. Theoretical background

2.1. Isothermal crystallization models

The crystallization process involves two consecutive steps, namely the formation and the subsequent growth of nuclei. When a polymer is super-cooled by lowering the temperature below the equilibrium melting point (T_m^0), nuclei appear

throughout the mass. They can appear instantaneously at the beginning of the process (instantaneous nucleation), or can appear in the liquid phase during the process (sporadic nucleation). The growth of nuclei occurs in either one, two or three directions, giving rise to rods, discs or spheres. Different models have been applied in order to quantitatively describe the macroscopic formation of the crystalline phase.

First of all, the classical theory of Avrami¹⁰ for phase transformation kinetics leads to the following simplified equation :

$$\alpha_f^c(t) = 1 - \exp(-k t^n) , \quad (1)$$

where α_f^c is the relative crystallinity degree (i.e. the ratio between the crystallized volume at time t and the total crystallizable volume) and k the kinetic constant (a function of the nucleation rate $\dot{N}$ and of the growth rate G). In this equation, the exponent n (called Avrami exponent) represents both the nucleation type (sporadic or instantaneous) and the number of growth dimensions. The value of n can be any positive integer between 1 and 4.

Billon and Haudin¹¹ have shown that the general approach of Avrami is totally equivalent with the generalized Evans model¹², which is based on the mathematical description of the expansion the waves created by droplets falling on the surface of a pool.

In most cases, the fitting of experimental data with the Avrami model leads to fractional values of the Avrami exponent (n), and to significant model deviations from the experimental data for long crystallization times. These observations are generally attributed to the simplified assumptions made in the Avrami model, namely :

- complete transformation of the sample;
- no volume change during phase transformation / crystallization;
- constant radial growth rate;
- uniqueness of nucleation;
- constant density and shape of the growing nuclei;
- no secondary crystallization.

Consequently, Eq. (1) leads to fractional values of n that cannot be explained on any physical basis. Therefore, an important effort has been spent to develop better models by relaxing one or several of the above assumptions.

Wunderlich¹³ and Lin¹⁴ have taken incomplete crystallization into account by introducing a new parameter (the ultimate degree of crystallinity of the sample α_v^∞) into the model. The Avrami / Evans equation is then completed as follows :

$$\alpha_v(t) = \alpha_v^\infty (1 - \exp(-k t^n)) \quad . \quad (2)$$

where α_v is the real degree of crystallinity.

Price¹⁵ and Mandelkern¹⁶ have introduced a difference of density between the amorphous and crystalline phases, in order to remove the isovolumic assumption. Kim and Kim¹⁷ have introduced a variable growth rate, while Banks and Sharples¹⁸ have considered a mixed mode of nucleation, where spherulitic growth simultaneously occurs from both instantaneously and sporadically originating nuclei.

In order to improve the Avrami model, Tobin¹⁹ has proposed a new expression for crystallization kinetics. The main difference between the Tobin and Avrami models concerns the assumption of growth site impingement. A summary of this theory is analysed in the Appendix. If one considers that the Avrami assumption is mathematically written as :

$$\frac{d\alpha_v^c}{dt} = (1 - \alpha_v^c) \frac{d\alpha_f}{dt} \quad , \quad (3)$$

where α_f is the fictive relative crystallinity degree (as calculated without taking impingement into account), the Tobin assumption can be summarized by the relation :

$$\alpha_v^c = (1 - \alpha_v^c) \alpha_f \quad . \quad (4)$$

Following this equation, at the end of the transformation, the volume of the whole crystalline entity will be 0. Due to this physical inconsistency, this model will not be considered further.

In fact, the crystallization of polymers is generally subdivided in three stages, owing to nucleation, and primary and secondary crystallization process. Primary crystallization is the main part of the whole process, while secondary crystallization

becomes dominant in the terminal stage. Secondary crystallization can be considered as to be simultaneous to, or consecutive to, primary crystallization for several reasons, such as lamellar thickening, crystallization of segregated molecules, or some kinds of reorganisation in already transformed portions. The analysis of crystallization is, in practice, quite complicated by the fact that primary crystallization is not readily separable from secondary crystallization in a theoretically meaningful way.

A model proposed by Hillier²⁰ and by Price²¹ considers the slow secondary crystallization occurring within a spherulite. Spherulites are assumed to first grow at a constant rate, following the exponential kinetics given by Eq. (1). Due to this first growth, crystallinity is thus assumed to increase from zero to $\alpha_v^{1,\infty}$, which is the degree of crystallinity at the end of the primary mechanism. Then, a slow secondary crystallization process starts within the occluded volume, and the total degree of crystallinity again increases by an amount $\alpha_v^{2,\infty}$ following the relation :

$$\alpha_v^2(t) = \alpha_v^{2,\infty} (1 - \exp(-k_2(t - \tau))) \quad (5)$$

Eq. (5) is in fact an Avrami equation, with a coefficient n_2 equal to 1 due to intra-spherulitic or interlamellar growth assumption. It gives the additional crystallinity at time t of elements of volume which have been included in the spherulites at time τ . Therefore, due to secondary crystallization, the density of the growing spherulites changes with time. The total crystallinity at time t is finally given by the so-called *integral model* :

$$\alpha_v(t) = \alpha_v^{1,\infty} (1 - \exp(-k_1 t^{n_1})) + \alpha_v^{2,\infty} \int_0^t \frac{\partial}{\partial \tau} (1 - \exp(-k_1 \tau^{n_1})) (1 - \exp(-k_2(t - \tau))) d\tau \quad (6)$$

where $\alpha_v^{1,\infty}$ and $\alpha_v^{2,\infty}$, k_1 and k_2 represent the final degrees of crystallinity and the rate constants due to primary and secondary crystallizations, respectively, while n_1 is the Avrami index for the first process. The presence of the integral leads to mathematical difficulties, which might hinder the analysis of experimental data.

Velisaris and Seferis²² have proposed an other way to consider secondary crystallization, by describing the time dependence of the crystallinity degree as a linear combination of two Avrami expressions, viz.:

$$\alpha_v^e(t) = \frac{\alpha_v(t)}{\alpha_\infty} = w_1 (1 - \exp(-k_1 t^{n_1})) + w_2 (1 - \exp(-k_2 t^{n_2})) \quad , \quad (7)$$

where $w_1 + w_2 = 1$. Such an expression, which is called the *parallel Avrami model*, corresponds to two different nucleation and growth processes, that occur in parallel. The relative importance of each process is expressed by the value of the weight factors w_1 and w_2 . When crystallization consists of a single mechanism, w_1 equals 1 and w_2 equals 0. Since the temperatures at which the first and second mechanisms are proceeding at a maximum rate may not be the same, w_1 and w_2 can vary with temperature. One may note that, in this model, the secondary process represents the total secondary crystallization due to inter- and intraspherulitic crystallization, without distinction between both processes. The main limitation of this model is that both mechanisms are independently considered, since both start at the same time. As the second mechanism represents a lamellar thickening effect, this assumption is wrong and the mechanisms must be consecutive.

A critical analysis of the fitting of experimental data with different models was undertaken by Ravindranath and Jog²³, who showed that the standard deviation is of the same order in magnitude for each model. They concluded that there is no universal approach and that different models must therefore be used in order to describe the crystallization of different polymers.

In all these models, the beginning of the crystallization process is used as a reference time. Between the beginning of a crystallization experiment and the emergence of the first crystalline nucleus, a certain duration however elapses, which is called the induction time. The latter may be considered as the only detectable macroscopic parameter which is representative of the nucleation process. As the induction time depends on the crystallization conditions, it is necessary to include this effect in the model. Consequently, a zero time reference that is independent of crystallization must be defined. On the basis of these considerations, we here propose a new model²⁴. Defining time $t=0$ as the beginning of the experiment, and introducing the induction times t_0^1 and t_0^2 for the first and second mechanisms, the

parallel model can be extended to provide what we call the *consecutive Avrami model* :

$$\alpha_v^c(t) = \frac{\alpha_v(t)}{\alpha_v^\infty} = w_1 (1 - \exp(-k_1 (t - t_0^1)^{n_1})) + w_2 (1 - \exp(-k_2 (t - t_0^2)^{n_2})) \quad (8)$$

Thanks to this method, the secondary crystallization process is certainly occurring well after the first one, because of the restriction $t_0^2 > t_0^1$.

2.2. Non-isothermal crystallization models

Nakamura *et al.*⁹ suggest a convenient procedure for using isothermal data for non-isothermal kinetics, on the basis of the following assumption : the rate of crystallization at time t only depends on the temperature and the relative crystallinity reached at that time, independently of the crystallization history. This involves the hypothesis that all isotherms at various temperatures can be transformed into a master curve when working with an appropriate reduced time²⁶. This assumption has allowed us to derive two methods for predicting non-isothermal crystallization kinetics based on the differential form of Eq. (1) :

$$\frac{D \alpha_v^c}{D t} = (1 - \alpha_v^c) [-\ln(1 - \alpha_v^c)]^{1-1/n} n k^{1/n} \quad (9)$$

A first method consists in considering the thermal history of the sample as successive isothermal steps, and in computing crystallization as a function of time. Defining an artificial time $\tilde{t}$ such that all the previous crystallization could equivalently occur isothermally at a fixed temperature;

$$\tilde{t}^{n(T)} = \frac{-\ln(1 - \alpha_v^c)}{k(T)} \quad , \quad (10)$$

one may develop the equations for the Avrami model leading to the system :

$$\begin{cases} \alpha_v^c(T_j) = 1 - \exp(-k(T_j) (\tilde{t}_{j-1} + \Delta t_j)^{n(T_j)}) \\ \tilde{t}_{j-1} = \sqrt[n(T_j)]{\frac{-\ln(1 - \alpha_v^c(T_{j-1}))}{k(T_j)}} \end{cases} \quad (11)$$

where T_j is the temperature during the interval $[t_{j-1}, t_j]$, with :

$$t_j = \sum_{n=1}^j \Delta t_n \quad (12)$$

The cooling history is here implicitly taken into account. Extension of this computational procedure to the consecutive isothermal model is complex, but numerically feasible. Induction time has to be handled with a special care.

The second method consists in integrating Eq. (9) with respect to time for temperature dependent k . It provides an integral model (which was first developed by Nakamura *et al.*⁹). One needs to use the isokinetic assumption and to keep the Avrami coefficient n constant. This leads to the following equation :

$$\alpha_v^c(T) = 1 - \exp \left(- \left(\int_{T_0}^T \frac{\sqrt[n]{k}}{\dot{T}} dT \right)^n \right) . \quad (13)$$

This non-isothermal model requires to know the value of the parameter n and the dependence of the kinetic function k with respect to temperature. In fact, at a constant cooling rate $\dot{T}$, this approach is equivalent to the Ozawa model²⁶, which is written as :

$$\alpha_v^c(T, \dot{T}) = 1 - \exp \left(- \frac{\chi(T)}{\dot{T}^n} \right) , \quad (14)$$

with $\chi(T) = \left(\int_{T_0}^T \sqrt[n]{k} dT \right)^n .$

The main limitations of the Ozawa model are that the cooling rate is kept constant and that it does not take into account any dependence of the ultimate degree of crystallinity upon thermal history. Nevertheless, extension to variable cooling rates has been carried out by Billon²⁷.

These non-isothermal models do not take induction time into account, which however represents an important effect. Patel and Spruiell⁸ have concluded that an overprediction of non-isothermal data can be attributed to the fact that traditional kinetic models do not account for this time. In order to determine when crystallization actually starts, the induction time function $t_0^i(T)$ will therefore be considered. Under non-isothermal conditions, the problem is however complicated. Sifleet²⁸ suggests that « during such a process, any amount of time spent at a temperature increases the relative completion of the induction time by the amount of that time divided by the induction time at that temperature ». When this cumulated

induction time factor (θ_i) reaches 1.0, induction is assumed to be complete and crystallization starts. Mathematically, this can be written as :

$$\theta_i = \int_0^{t_0^{i*}} \frac{1}{t_0^i(T)} dt \quad , \quad (15)$$

and crystallization begins at time t_0^{i*} . It is therefore possible to define the induction time for both isothermal and non-isothermal crystallization conditions.

On the basis of the above considerations, we have extended our consecutive isothermal model to non-isothermal processes by using the same approach as Nakamura *et al.*⁹:

$$\begin{aligned} \alpha_v(t) = & \int_0^t \alpha_v^\infty w_1 \frac{\partial}{\partial \tau} \left(1 - \exp \left(- \left[\int_{t_0^{1*}}^\tau \sqrt[n_1]{k_1} ds \right]^{n_1} \right) \right) d\tau \\ & + \int_0^t \alpha_v^\infty (1-w_1) \frac{\partial}{\partial \tau} \left(1 - \exp \left(- \left[\int_{t_0^{2*}}^\tau \sqrt[n_2]{k_2} ds \right]^{n_2} \right) \right) d\tau \quad .(16) \end{aligned}$$

The differential of each mechanism is multiplied by the ultimate ratio α_v^∞ and by the associated weights w_1 or $1-w_1$, and is then integrated with respect to time in order to take the temperature dependence of α_v^∞ and w_1 into account. Symbols t_0^{1*} and t_0^{2*} represent the non-isothermal induction times calculated by means of Eq. (15).

3. Experimental

Crystallization kinetics of PET have been carried out using a Perkin-Elmer DSC2B differential scanning calorimeter, equipped with a thermal analysis data station. The equipment calibration was performed using Indium and Zinc as standard materials. In order to simplify the analyses, data were transferred to a Macintosh computer where the IGOR[®] software was used for numerical treatments.

The samples were a grade of PET, namely PET A02-304, supplied by AKZO (Mn $\approx$ 20000). In polycondensates, moisture has a great influence on crystallization,

since it reduces molecular weight by hydrolysis and thus increases the nucleation rate. The samples were thus held 8 hours at 120°C under vacuum, in order to remove absorbed moisture. To avoid thermal degradation of the polymer, a new sample was used for each thermal cycle, and experiments were carried out under nitrogen atmosphere. In order to keep a good signal/noise ratio and, at the same time, to limit the instabilities due to thermal inertia, masses of about 6 to 10 mg were used in the DSC apparatus.

Isothermal crystallization exotherms were obtained over a temperature range of 175-235 °C from the molten state, and of 120-165°C from the glassy state since it was not possible to quickly enough reach these temperatures from the melt state before crystallization starts. Before recording the exotherms, the samples were heated up to 280°C and held at that temperature for 3 min., in order to ensure complete melting of the polymer. Then, these samples were rapidly cooled (320°C/min) at a constant test temperature for obtaining an isothermal crystallization from the molten state. For experiments from the glassy state, the samples were quenched below T_g and then rapidly heated (320°C/min) to the test temperature.

The same melting history has been used for non-isothermal experiments. In that case, recorded temperatures must be corrected in order to take the temperature lag between the sample and the furnace into account. The correction factor can be determined by measuring the melting or crystallization of Indium as a function of the temperature ramp²⁹. Thanks to this technique, accurate data could be obtained at cooling rates up to 40°C/min. A more accurate analysis of non-isothermal DSC curves has been recently suggested by Janeschitz-Kriegl *et al.*^{30,31}, whose method is based on the calibration of the heat transfer coefficient between the pan and the sample (which is non negligible for high cooling rates).

A typical DSC curve, as obtained after the heating of an amorphous sample, is shown in Fig. II.1. Note that PET materials have a T_g of 80°C and a T_m around 260°C.

3.1. Kinetics measurements

The crystallization kinetics were obtained by integrating crystallization peaks from the DSC thermogram, assuming a proportionality between the crystallization rate and the heat flux measured by DSC. This curve actually represents a relative transformation rate, $\alpha_w / \alpha_w^\infty$, which is ranging from 0 to 1 and is proportional to the crystallized mass. Because the previously developed models have been expressed in terms of volume fraction, it is necessary to transform the weight fraction into a volume fraction. This can be done by using the following relation :

$$\alpha_v = \frac{\frac{\rho_a}{\rho_c} \alpha_w}{1 - \left(1 - \frac{\rho_a}{\rho_c}\right) \alpha_w} \quad , \quad (17)$$

where ρ_a and ρ_c are the densities of a 100% amorphous sample a 100% crystalline sample, respectively 1.335 and 1.455 for PET³². The volumic kinetics is then obtained from the weight kinetics thanks to the following relation :

$$\alpha_v^c = \frac{\alpha_w^c \left[1 - \left(1 - \frac{\rho_a}{\rho_c}\right) \alpha_w^\infty\right]}{1 - \left(1 - \frac{\rho_a}{\rho_c}\right) \alpha_w^\infty \alpha_w^c} \quad , \quad (18)$$

which gives the relative volume fraction that has been transformed during the experiment, and is going from 0 to 100%. This ratio does not give the absolute volumic degree of crystallinity, which in fact can be obtained by multiplying α_v^c by α_v^∞ , this latter being derived from α_w^∞ by using Eq. (17).

3.2. Determination of the ultimate crystallinity degree

When an amorphous PET sample is heated in a DSC, a first peak at 130-140°C, corresponding to a crystallization on heating (subscripts *ch*), is generally observed on the thermogram (Fig. II.1a). This crystallization is characterised by means of a temperature T_{ch} and a heat flux ΔH_{ch} . Then, at about 240°C, polymer crystals start to melt; the melting peak is characterised by parameters T_m and ΔH_m . Theoretically, as the melting and crystallization heats are directly proportional to the transformed mass, the difference $\Delta H_m - \Delta H_{ch}$ is proportional to the degree of crystallinity in the polymer at the beginning of the experiment. The ratio between

this difference and the melting heat of a pure crystal, ΔH_m^0 , will thus give the initial massic degree of crystallinity of sample :

$$\alpha_w^\infty = \frac{\Delta H_m - \Delta H_{ch}}{\Delta H_m^0} . \quad (19)$$

A careful examination of the thermogram leads to the assumption that crystallization on heating does not limit itself to the visible peak, but weakly continues until melting starts. There is an imperceptible, but non negligible heat flux. Thus, Eq. (19) generally leads to false results, and the error is even more pronounced for a more amorphous polymer. Several searchers³³³⁵, who have worked on this problem, have proposed to study the crystallinity rate of a sample by means of a unique base line, as shown in Fig. II.1b. The difference Δh between melting and crystallization enthalpy can then be calculated. Its value is related to the initial crystallinity rate by the following relation :

$$\alpha_w^\infty = \frac{\Delta h}{\Delta H_m^0} . \quad (20)$$

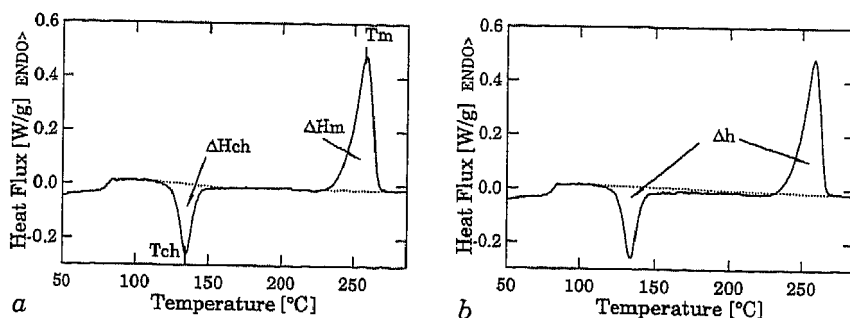


Figure II.1 : Typical DSC curve of a PET sample on heating (10°C/min). a) computation of phase transformation enthalpies by means of visible peaks, b) direct computation of the difference between the phase transformation enthalpies.

This method requires very accurate DSC experiments, because a small curvature in the baseline would induce errors. It still remains an approximation, because changes of the specific heat with temperature and with the nature of the material (amorphous, crystalline, ...) are not taken into account. However, this approach correlates very well with values obtained by density and IR measurements²⁴ when

using a value of 100 J/g for ΔH_m^0 which corresponds to the value experimentally determined by Van Antwerpen³⁶.

4. Computational procedure

There are several ways to calculate the parameters n and k of the Avrami equation²⁴. We have concluded that the best method for determining the material data of our consecutive isothermal crystallization model was the use of a non-linear regression in the (non-log) diagram (α_v^c, t) . The Levenberg and Marquard non-linear multivariable regression method³⁷ was thus used to analyse the isothermal experimental results.

Another method, used by Douillard *et al.*³⁸, consists in reconstructing isothermal parameters from non-isothermal experiments, by directly using the relations between the isothermal and non-isothermal models. The advantage of this approach is that a few number of non-isothermal experiments (which are the easiest to perform) will give parameters in a broad temperature range. Unfortunately, this procedure cannot be used for our complex model (with its two mechanisms, and for which parameters α_v^∞ , w_1 and w_2 are functions of temperature). It however remains a convenient approach when only one crystallization mechanism is considered.

Induction time is probably the most difficult parameter to determine. Indeed, because of the fast cooling or heating of the sample to crystallization temperature, a strong instability is observed at the beginning of an isothermal experiment, which interacts with crystallization. Therefore, it seems impossible to accurately measure the induction time, which, as will be seen later, is however of major importance for the determination of the parameters n and k in the Avrami equation. For a same experiment, one can indeed observe in Fig. II.2 high variations of the kinetic curve with different choices of t_0^1 .

First of all, a reference time must be chosen, which must be independent of the crystallization process. We have chosen the time at which the isothermal condition is reached. It corresponds to the equilibrium temperature in the DSC cell.

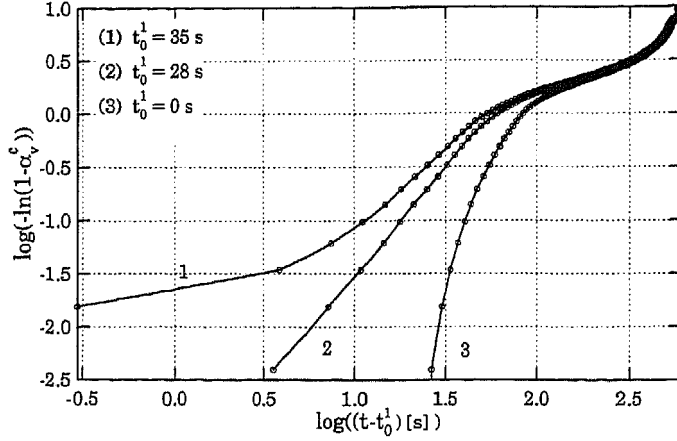


Figure II.2 : Experimental results of isothermal crystallization of PET at 473 K. Influence of the induction time t_0^1 on the crystallization kinetics.

For characterizing the beginning of crystallization, some authors choose the beginning of the crystallization exotherm peak, while some other authors select the onset of this peak. However, the accuracy of these values is generally bad, because of non-isothermal instabilities. Other workers therefore select the time at which the apparatus is in isothermal equilibrium (curve 2 in Fig. II.2), or the time corresponding to the intersection between the extrapolation of the DSC curve after crystallization and the same curve before crystallization (curve 1 in the same figure). From this, it should be concluded that the methods devoted to determine the beginning of crystallization are very arbitrary. To avoid such problems, we have preferred to use an extrapolation method, which consists in extracting the first 30% from each crystallization curve and fitting this curve by an Avrami equation that includes induction time :

$$\alpha_v^c(t) = 1 - \exp(-k(t-t_0^1)^n) \quad . \quad (21)$$

An approximate value of t_0^1 is obtained in this way (curve 3 in Fig. II.2). This method corrects the first bad data due to instabilities, by the means of more accurate values obtained later in the thermogram. The choice of the 30% value is quite arbitrary, but this allows to consider only one crystallization mechanism in the computation. This numerical way of determining the induction time is more efficient than the direct

calculation of all the parameters of the consecutive model by the least square method. Indeed, the number of parameters to be determined afterwards is reduced by 1, which is numerically more stable because there is no possibility to invert the two mechanisms.

5. Results and discussion

5.1. Limitation of the fitting method

In some cases, the simple Avrami equation is appropriate to describe the crystallization process. However, numerical analysis shows that this equation may fit the experimental results with a quite large range of imposed values of n . For example, giving to n the successive values 1, 2, 3 and 4, it is observed that coefficients t_0^1 and k progressively decrease to compensate for the rise of n , in order to keep the general shape of the curve unchanged (Fig. II.3, Table II.1).

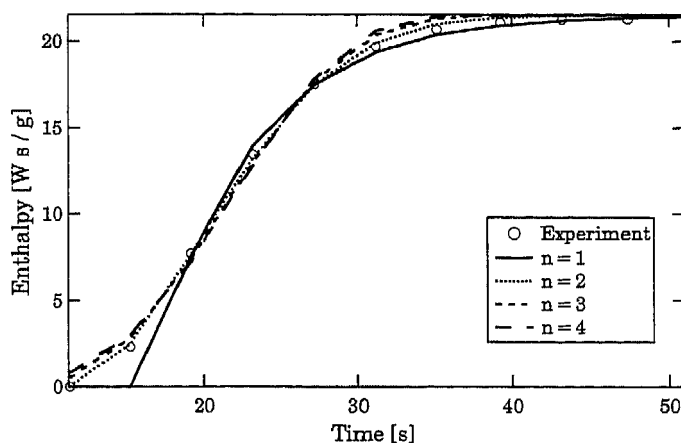


Figure II.3 : Crystallization of PET at 433 K. Avrami modelling for 4 different values of n .

It is also possible to keep $n=3$, and to let the induction time t_0^1 , which is now imposed, vary from 0 to 10 seconds, while k is calculated to obtain the best fit (Fig. II.4, Table II.2). This latter table provides a quantitative measurement of the

above mentioned errors (see Fig. II.2). A fairly high indeterminacy of the parameters of the Avrami equation is therefore observed. He and Zoller³⁹ recently reported similar results concerning the impact of the induction time on the Avrami coefficient. The importance of a very accurate determination of the induction time should however again be stressed.

Table II.1

Parameters k and t_0^1 as estimated when imposing $n = 1, 2, 3$ or 4 .

n	1	2	3	4
k	1.53e-1	6.01e-3	1.75e-4	3.68e-6
t_0^1	16.3	10.6	5.79	0.916

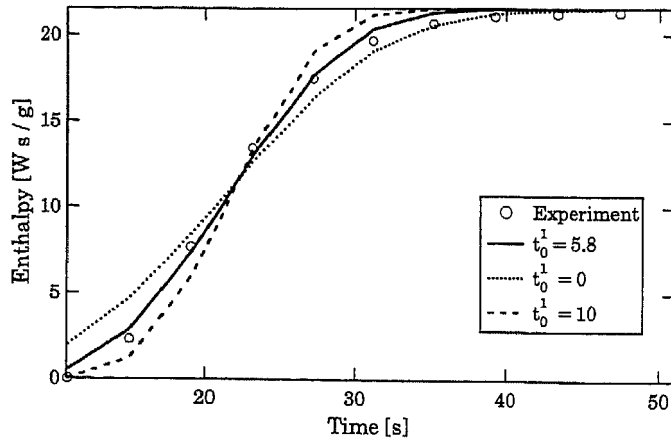


Figure II.4 : Same case as in Fig. II.3. Avrami modelling with $n = 3$ and 3 different induction times.

Table II.2

Parameter k , as estimated by a best fit when imposing $n = 3$ and $t_0^1 = 0, 5.8$ or 10 s.

t_0^1	0.00	5.79	10.0
k	7.08e-5	1.75e-4	4.22e-4

The Avrami model is therefore theoretically coherent, but leads to a kinetic equation which is difficult to analyse from a numerical as well as experimental viewpoint. Its principal limitation lies in the important indeterminacy of the governing parameters, which suggests that any physical conclusion that can be drawn from a given value of these parameters, as is sometimes found in literature, may be easily corrupted by the fitting procedure. Recently, Hammami and Mehrotra⁴⁰ have re-examined a model proposed by Choe and Lee⁴¹ and obtained a similar conclusion : « ... The above findings depict the disadvantage and the risk involved in using non linear regression technique to fit theoretically derived models to experimental data. In most instances, one can fit empirical models with few adjustable parameters to any set of data, yet in the majority of such cases, the obtained parameters possess no physical meanings ».

This conclusion has led us to fix the value of some selected parameters, in order to minimize the numerical indeterminacy between the parameters obtained from different experiments. The first induction time is always fixed by means of the above described method. Moreover, when using the Nakamura model, the value of the Avrami coefficient is also kept constant (as it should be). Finally, the value of n is imposed for the two mechanisms. For the primary mechanism, a value of 3 is imposed which, according to the Avrami theory, represents a crystallization with 3D growth and instantaneous nucleation, as it is often reported in literature. Optical microscopy experiments confirm the assumption of spherulitic growth for crystallization from quiescent melt²⁴. For the secondary process, a value of 1 is chosen, which corresponds to a 1D lamellar thickening, as it is often observed for this mechanism, see Hillier²⁰.

5.2. Comparison between the different isothermal models

In Fig. II.5, the crystallization kinetics of PET at 200°C is represented using the Avrami model (Eq. 1), the integral model (Eq. 6), the parallel model (Eq. 7) and our consecutive model (Eq. 8). As far as the Avrami model is concerned, deviations are observed for long crystallization times, as it is widely mentioned in literature.

The best results are provided by the integral model, which is however difficult to use (especially when the aim is to simulate the moulding process) due to the presence of a time integral. In the parallel model, the assumption that the secondary process begins at the same time as the first one is not physically acceptable. Moreover, the secondary process is modelled as being more important than the first one at the start-up of the process. The main advantage of this model is that no integral has to be evaluated.

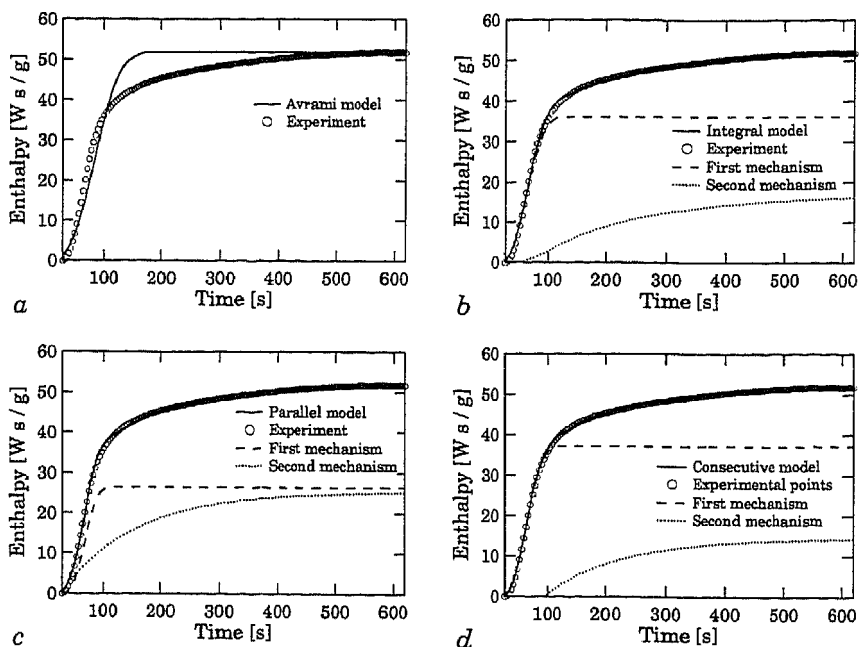


Figure II.5 : Crystallization of PET at 433 K. a. Avrami model; b. integral model; c. parallel model; d. consecutive model.

Our model rests on a double advantage, since it combines the simplicity of the parallel model and the physical coherence of the integral model, because secondary crystallization effectively starts after primary crystallization.

5.3. The consecutive Avrami model

The parameters of the consecutive model have been calculated on the basis of experimental results obtained in isothermal conditions. Thermogram data were first processed as previously described, while parameters resulting from regression analysis were obtained for different crystallization temperatures. In a second step, the dependence of these parameters with respect to crystallization temperature was determined by non-linear regression. A judicious mathematical representation for this functional dependence was thus required.

Note that, as above explained, the parameters n_1 and n_2 are held constant (with the values 3 and 1, respectively). Except for very slow crystallization, fixing these parameters does not introduce important errors in comparison with a simulation with varying parameters²⁴.

Parameter w_1 represents the ratio between the first crystallization mechanism and the global phenomenon. In Fig. II.6, this fraction is observed to vary with crystallization temperature in a non negligible way, and seems to tend to 1 at both extremities of the temperature interval.

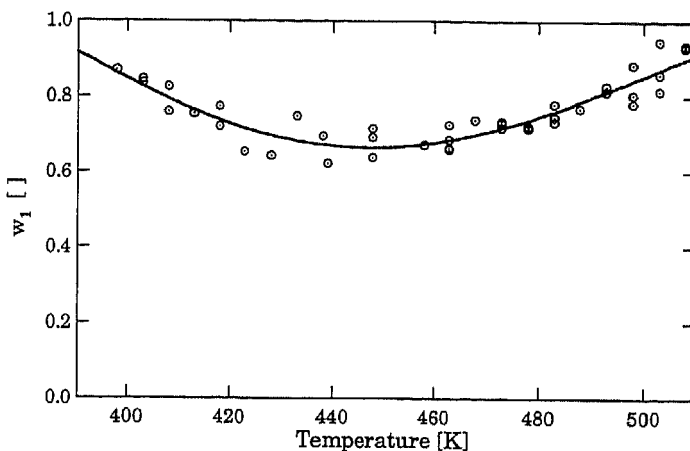


Figure II.6 : Dependence of the non-dimensional parameter w_1 with respect to crystallization temperature. Experimental data and model results by use of Eq. (22).

This parameter w_1 cannot be held constant, but no theory was found as far to predict its temperature dependence. The interpolation function was therefore arbitrarily chosen. At temperatures T_m^0 and T_g , w_1 was imposed equal to 1, meaning that crystallization is governed by the first mechanism only. This makes sense, since the process develops very slowly at a temperature close to T_m^0 or T_g . Macromolecules have time enough to move and rearrange in order to provide an optimal crystal configuration without requiring secondary crystallization. The following equation was thus used to approximate w_1 :

$$w_1 = 1 - a \exp\left(-\frac{b}{T - T_g}\right) \exp\left(-\frac{c}{T_m^0 - T}\right) \quad , \quad (22)$$

where a , b and c are fitting coefficients ($a = 4.737$, $b = 113.73$ and $c = 162.51$).

Parameters k_1 and k_2 are strongly temperature dependent as shown in (Figs. II.7 and II.8). A maximum is observed at approximately $(T_m + T_g)/2$. A higher dispersion of the values of k_1 is observed for temperatures below 440 K than for temperatures above 440 K. In fact, below 440 K, the crystallization experiments were carried out from the amorphous state under T_g and the dispersion is due to the non-homogeneity of the quench preceding the experiment.

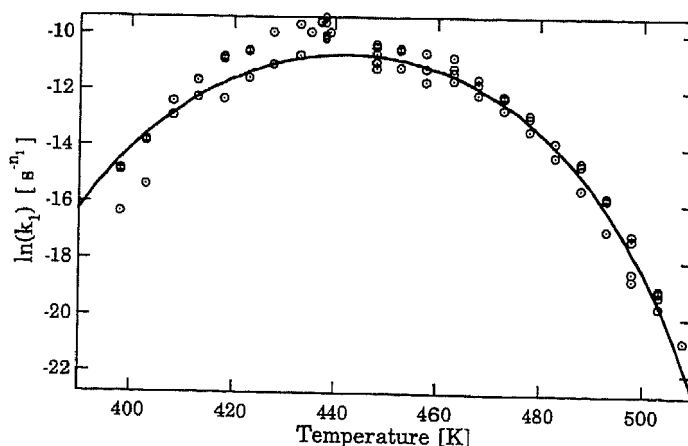


Figure II.7 : Dependence of the parameter k_1 with respect to crystallization temperature. Experimental data and model results by use of Eq. (23).

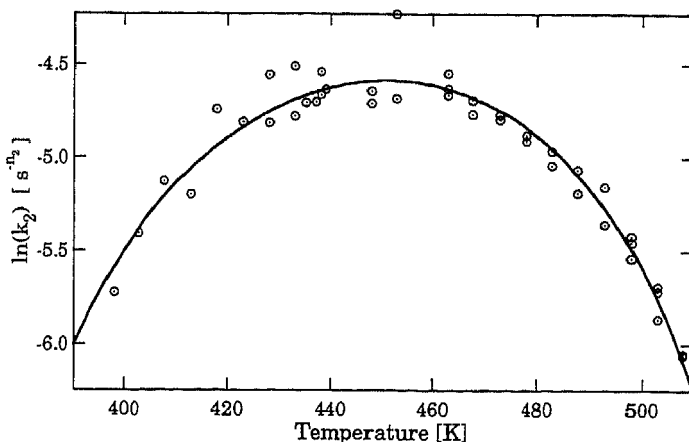


Figure II.8 : Dependence of the parameter k_2 with respect to crystallization temperature. Experimental data and model results by use of Eq. (23).

Following the Avrami theory, these parameters are related to the crystallization growth rate G_i . The interpolation function selected to represent their dependence with respect to temperature was therefore based on studies of Van Antwerpen³⁸ on the growth rate. The following equation was used for k_1 and k_2 :

$$k_i = a_i^k \exp\left(-\frac{b_i^k}{T - T_g + 24}\right) \exp\left(-\frac{c_i^k}{T^2(T_m^0 - T)}\right), \quad (23)$$

where, a_i^k , b_i^k , c_i^k are fitting coefficients which are given in Table II.3.

Table II.3

Parameters for the functions k_1 and k_2 .

	a_i^k	b_i^k	c_i^k
k_1	$8.466 \cdot 10^7$	$1.021 \cdot 10^3$	$4.601 \cdot 10^8$
k_2	1.688	$2.293 \cdot 10^2$	$7.159 \cdot 10^7$

Figs. II.9 and II.10 represent the induction times t_0^1 and t_0^2 , which seem to tend to infinity at T_g and T_m^0 . As the induction time is representative of the nucleation process, its dependence with respect to temperature can be deduced from the temperature dependence of the nucleation rate. Following the general approach

reported in literature for nucleation and crystal growth, the temperature dependence of the induction time can thus be given by the following relation, which has appropriate asymptotes at T_g and T_m^0 :

$$t_0^i = d_i \exp\left(\frac{e_i}{T - T_g}\right) \exp\left(\frac{f_i}{T_m^0 - T}\right), \quad (24)$$

where d_i , e_i , f_i are tabulated in Table II.4.

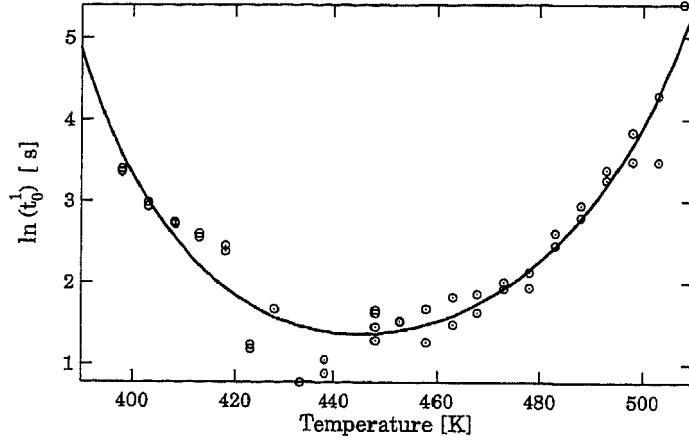


Figure II.9 : Dependence of the induction time t_0^1 with respect to crystallization temperature. Experimental data and model results by use of Eq. (24).

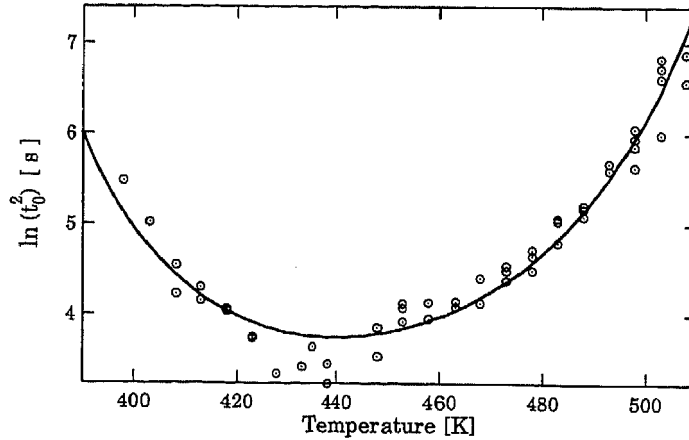


Figure II.10 : Dependence of the induction time t_0^2 with respect to crystallization temperature. Experimental data and model results by use of Eq. (24).

Table II.4
Parameters for the functions t_0^1 and t_0^2

	d_i	e_i	f_i
t_0^1	$2.480 \cdot 10^{-3}$	$2.997 \cdot 10^2$	$4.724 \cdot 10^2$
t_0^2	$1.295 \cdot 10^{-1}$	$2.097 \cdot 10^2$	$4.056 \cdot 10^2$

The ultimate crystallinity degree α_v^∞ is represented in Fig. II.11 versus crystallization temperature. A constant increase with temperature is observed, which can be explained by the important mobility of the macromolecules and their ease to arrange themselves into a crystalline network at higher temperature. A cubic interpolation function was used :

$$\alpha_v^\infty = \left(\frac{T - T_g}{100} \right) \left(\frac{100}{T_m^0 - T_g} - g(T_m^0 - T) - h(T_m^0 - T)^2 \right) , \quad (25)$$

where g and h are $-2.6216 \cdot 10^{-2} \text{ K}^{-2}$ and $2.6024 \cdot 10^{-5} \text{ K}^{-3}$, respectively. This function has not any physical basis, but is a good representation of reality. It imposes α_v^∞ equal to 0 when $T = T_g$, and to 1 when T is the thermodynamic melting temperature.

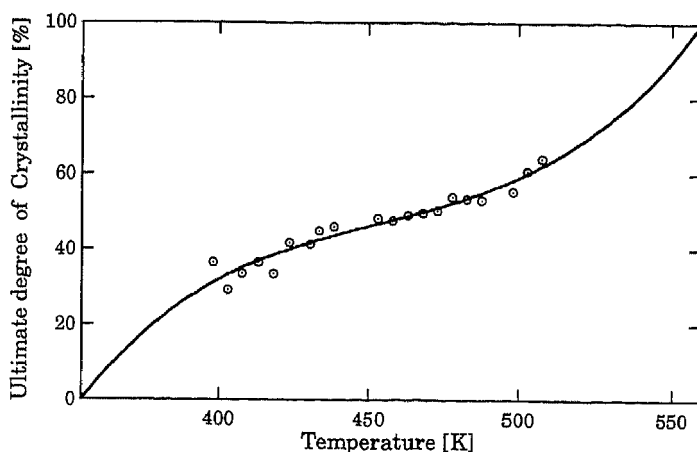


Figure II.11 : Dependence of the ultimate crystallinity degree with respect to crystallization temperature. Modelling by means of a cubic polynomial.

In order to ensure that the consecutive Avrami model is of practical use when these interpolation functions are introduced, experimental and model results were compared. The complete kinetic model obtained with the parameters computed by least-square regression is represented in Fig. II.12 for some fixed temperatures. A reasonable agreement is found between experimental and predicted curves.

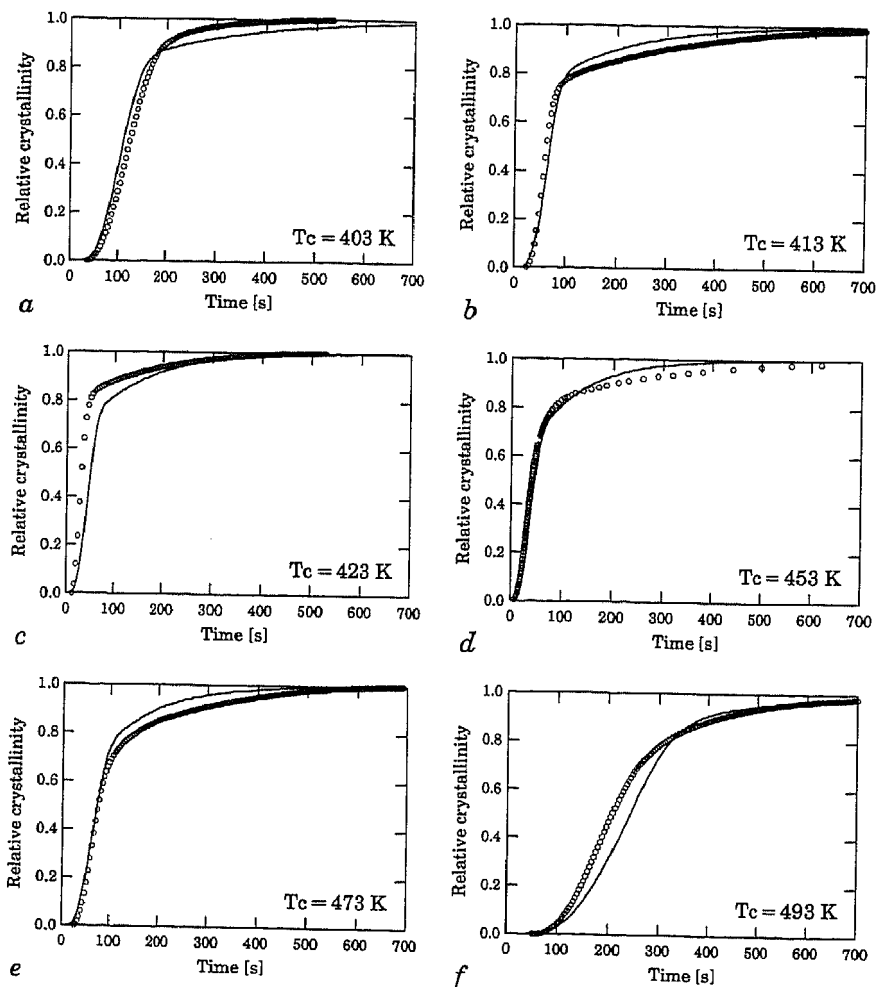


Figure II.12: Comparison between isothermal crystallization experiments (markers) and consecutive model predictions (lines) for different crystallization temperatures : *a*, $T_c = 403$ K; *b*, $T_c = 413$ K; *c*, $T_c = 423$ K; *d*, $T_c = 453$ K; *e*, $T_c = 473$ K; *f*, $T_c = 493$ K.

Small discrepancies arise from the dispersion of the parameters obtained from each isothermal experiment. Having in mind the difficulty of the experimental measurement of crystallization kinetics (in view of thermal instabilities, noise on the DSC, complex choice of a baseline, ...), and the numerical problems related to the fitting technique (and, in particular, the important indeterminacy of the parameters), the results obtained with our new model are quite satisfactory in a large crystallization temperature range.

5.4. Non-isothermal kinetics

The isothermal parameters obtained in the previous section can be used to predict the non-isothermal crystallization behaviour of PET by means of the modified Nakamura model (Eq. 16). Fig. II.13 compares this model with corresponding experiments. Our consecutive model perfectly describes the global evolution of crystallinity in the sample. A correct estimation of the starting temperature and the final crystallinity rate is obtained, together with a good estimation of the importance of the first crystallization mechanism with respect to the second one. At large cooling rates, the second mechanism does not have time enough to start.

Fig. II.14 shows the effect of cooling rate upon the final degree of crystallinity in PET samples. Four distinct behaviours are observed, which can easily be explained by means of Fig. II.15, where real crystallinity and relative crystallinity degrees are depicted for both mechanisms. At very high cooling rates (> 10 K/s), no crystallization is observed, since the sample is quenched. At lower cooling rates, crystallinity is only due to primary crystallization, while secondary crystallization has not enough time to start. At still lower cooling rates, secondary crystallization takes place when primary crystallization is almost complete. However, the crystalline perfection of the spherulites formed during primary crystallization is higher when the cooling rate is lower. At the lowest cooling rates, both mechanisms are complete and only crystalline perfection can increase the final degree of crystallinity, while the secondary mechanism has a lower impact on the global crystallinity. This behaviour results from the evolution of the final degree of crystallinity, which increases when temperature increases, and of the weight fraction

of the primary mechanism, which also becomes more important at a higher temperature (Figs. II.6 and II.11). Indeed, as the cooling rate is decreasing, the temperature at which crystallization starts becomes higher, and an increase of final crystallinity degree is predicted.

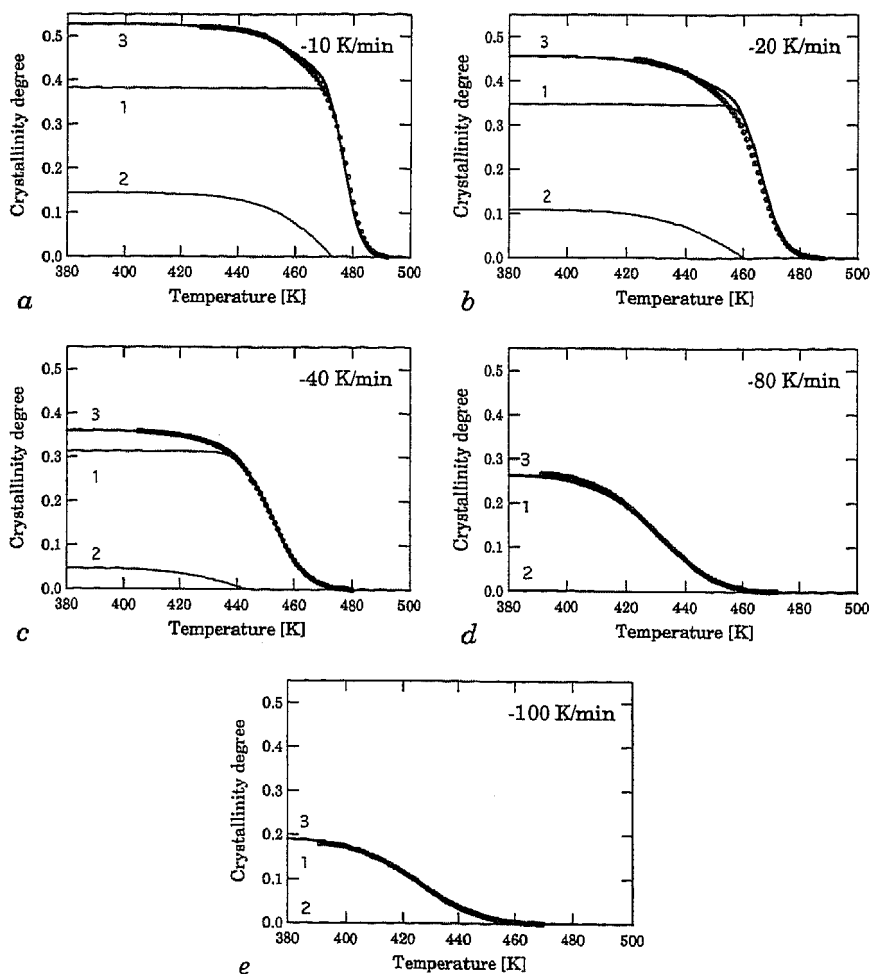


Figure II.13: Comparison between experimental non-isothermal crystallization experiments (markers) and model predictions (1, 1st mechanism; 2, 2nd mechanism; 3, global kinetics) for several constant cooling rate: a, -10 K/min; b, -20 K/min; c, -40 K/min; d, -80 K/min; e, -100 K/min.

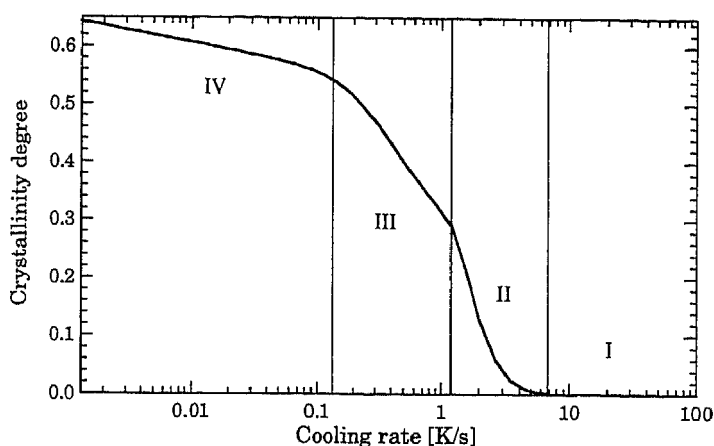


Figure II.14: Prediction of crystallinity as a function of cooling rate, by means of the extended Nakamura model.

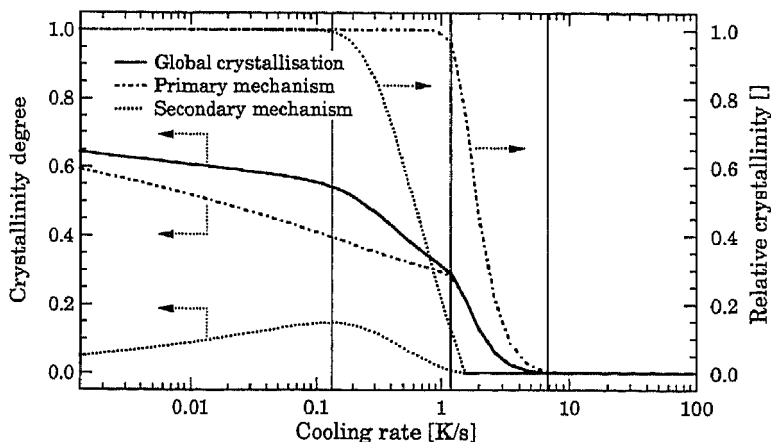


Figure II.15: Prediction of crystallinity and relative crystallinity degrees as a function of cooling rate for both primary and secondary mechanisms. Comparison with the global crystallinity.

This behaviour can be related to the experiments of Brucato *et al.*⁴², who carried out density measurement of PET samples cooled at various rates (Fig. II.16). Comparing these results with density prediction from our model shows a good qualitative agreement.

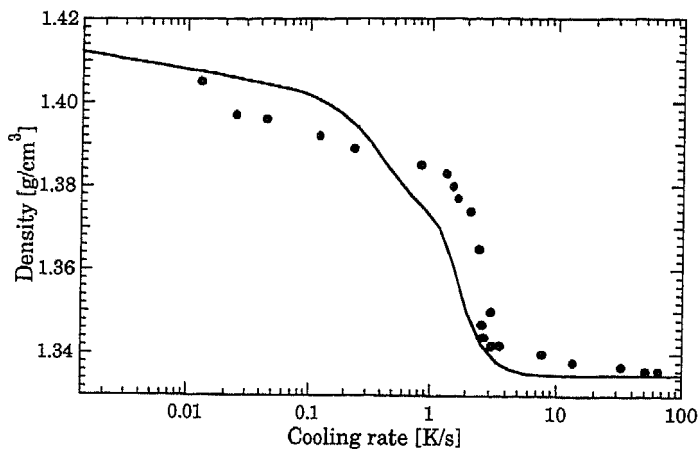


Figure II.16: Comparison between density prediction as a function of cooling rate and the experimental results of Brucato et al.²

6. Conclusions

We have developed a new crystallization model, namely the consecutive Avrami model, which is valid in both isothermal and non-isothermal conditions. This model, which takes into account ultimate crystallinity degree, induction time and secondary crystallization, was first developed for PET, but can also be applied to other high T_g polymers having similar behaviour.

Determining the parameters of this model was carried out through isothermal crystallization kinetic experiments with a DSC apparatus. From these parameters, interpolation functions were obtained which, when being combined with our consecutive model, allow for the prediction of isothermal crystallization kinetics. Introducing these interpolation functions into the extended Nakamura model allows for the prediction of non-isothermal crystallization kinetics. Agreement between experimental results and numerical predictions is observed. The model is able to accurately predict the ultimate crystallinity degree for any thermal history. Moreover, a good agreement is obtained with respect to the beginning of crystallization and the shape of the crystallization kinetics.

Appendix

The Tobin theory can be summarized as follows. In the case of non-impingement, the kinetics of phase transformation for a 2D system with sporadic nucleation is written as :

$$\alpha_f(t) = \dot{N} G \int_0^t (t-\tau)^2 d\tau = k t^3 \quad , \quad (26)$$

where $\alpha_f(t)$ is the extended fraction of the total surface transformed at time t , $\dot{N}$ is the number of nuclei appearing per unit area and time, and where $G(t-\tau)^2$ is the area at time t of the entities created at time τ . Up to this point, this is exactly the Avrami development.

As growth proceeds, two perturbing phenomena develop. First, the net nucleation rate decreases owing to solidification of the molten phase. Second, the individual growth sites impinge, in such a way that the net growth rate of any given site eventually decreases. Tobin's development differs from the Avrami approach by the way these two phenomena are taken into account.

Only the true nucleation rate is considered, and the number of new nucleation sites formed in the interval $d\tau$ around τ is

$$dn = \dot{N} (1 - \alpha_g(\tau)) d\tau \quad , \quad (27)$$

while the total area transformed at time t is given by the formula :

$$\alpha_g(t) = \dot{N} \int_0^t f(t, \tau) (1 - \alpha_g(\tau)) d\tau \quad . \quad (28)$$

Here, $f(t, \tau)$ is the area occupied at time t by the entities created at time τ , taking impingement into account. The heart of the problem consists in getting a mathematical expression for this latter effect.

Following Tobin, a useful approach may be deduced from the consideration of a simple limiting case. «the nuclei are formed homogeneously at random, grow instantaneously to a fixed area X , then stop growing». Impingement is modelled by assuming that «each new growth site makes an average contribution $X(1 - \alpha_g(\tau))$ to the total area. This is to say that because of impingement, each new site can

contribute to the total area only that fraction of its area corresponding to the net free area remaining at time τ . » This leads to the following equation :

$$d\alpha_v^c = \dot{N} X (1 - \alpha_v^c(\tau))^2 d\tau \quad , \quad (29)$$

which, after integration, gives :

$$\frac{\alpha_v^c}{1 - \alpha_v^c} = \dot{N} X t \quad . \quad (30)$$

Applying this assumption to crystallization, Tobin writes : « We will proceed ... by assuming that at time t , a growth site formed at an earlier time τ occupies an area :

$$(1 - \alpha_v^c(t)) G(t - \tau)^2 \quad . \quad (31)$$

This is to say that each growth site has its effective area at time t reduced by the same fraction, regardless of when it was formed. » From Eqs. (28) and (31) (which provides $f(t, \tau)$), this approach gives the following equation :

$$\alpha_v^c(t) = \dot{N} \int_0^t (1 - \alpha_v^c(t)) G(t - \tau)^2 (1 - \alpha_v^c(\tau)) d\tau \quad , \quad (32)$$

$$\text{and} \quad \frac{\alpha_v^c(t)}{1 - \alpha_v^c(t)} = \dot{N} G \int_0^t (t - \tau)^2 (1 - \alpha_v^c(\tau)) d\tau \quad , \quad (33)$$

which expresses α_v^c as the solution of a non linear Volterra integral equation. A zero-order approximation of α_v^c is given by :

$$\frac{\alpha_v^c(t)}{1 - \alpha_v^c(t)} = k t^3 \quad , \quad (34)$$

which can be extended to other geometries and nucleation mechanisms in the form :

$$\frac{\alpha_v^c(t)}{1 - \alpha_v^c(t)} = k t^n \quad . \quad (35)$$

In fact, we believe that the impingement mechanism proposed by Tobin is excessive. This approach is correct indeed for his simplified model case, with instantaneous growth and constant area of the growth sites, but it ends in exactly the same result as the Avrami model does if all the nuclei are taken into account. Letting the crystalline entities grow by use of Eq. (31) tends to change the area of the grown phase proportionally to the remaining area. This would mean that, at the end

of the transformation, the area of each crystalline entity would tend to 0, which is physically unacceptable. Tobin's extrapolation from a simplified model case to polymer crystallization is, therefore, physically unacceptable.

The interest of Tobin's equation lies in the fact that it is the first order Taylor development of the Avrami equation around 0. Indeed,

$$(1 - \alpha_v^c) \ln(1 - \alpha_v^c) = -\alpha_v^c, \quad (36)$$

which, combined with Eq. (1), gives Eq. (35). In Fig. II.17, a comparison between the Avrami equation and its first and second order Taylor developments is shown. For a short time t , i.e. for small values of α_v^c , Eq. (35) is very close to Eq. (1). After a long time however, α_v^c approaches 1 faster with the Avrami model than with Tobin's equation. This explains why Tobin's equation was generally found to be suitable for experimental data up to higher value of α_v^c than the Avrami model.

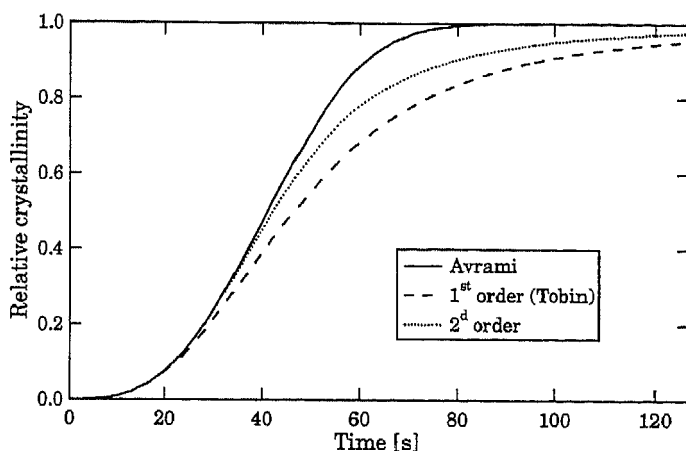


Figure II.17: Comparison between the prediction of the Avrami model, of its first order Taylor development (which is Tobin's equation) and of its second order development, for of $k=1e-5$ and $n=3$ (arbitrary value).

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Chapter III

Shear-Induced Crystallization Kinetics of PET : Development of a Mathematical Model adapted to Numerical Predictions in Polymer Processing Simulation

Abstract

Although shear-induced crystallization has been extensively studied in the past, there remains nowadays an important interest in the development of an accurate model able to predict crystallization during injection moulding, where shear flows dominates. In this study, we investigate the shear-induced crystallization of polyethylene terephthalate (PET), by combining both experimental measurements and mathematical modelling. The physical model is based on the consecutive Avrami model, which is suitable to describe isothermal and non-isothermal crystallization kinetics of PET. This model includes the effects of induction time, final degree of crystallinity and the presence of a secondary crystallization mechanism. As the Avrami model, it describes the crystallization rate through a kinetic parameter, which is a function of both nucleation and crystal growth processes. However, in order to correctly handle shear-induced crystallization, these fundamental processes must be governed by distinct parameters. An improved model is therefore proposed. Crystallization under shear is analysed through viscosity measurements of a sheared PET melt in a cone and plane rheometer, from which shear-induced crystallization kinetics are deduced, allowing for the determination of the shear dependency of the parameters. The new model is validated by means of comparisons with experiments obtained in a wide range of thermal and shear conditions.

1. Introduction

The kinetics and mechanisms of polymer crystallization and the resulting crystalline morphologies have been the focus of much scientific attention. This latter results from the fact that the properties of manufactured products strongly depend upon crystallinity, which is in turn governed by the temperature, shear and pressure conditions under which the polymer is processed.

The present work has been undertaken in order to introduce the crystallization phenomena into an injection moulding simulation software (*MOLDSYS*), developed by Dupret and his group¹⁷. The injection moulding process is characterized by a time-dependent non-isothermal flow in thin cavities, in which shear-flow dominates. In the case of semi-crystalline polymers, it is expected that shear-induced crystallization plays an essential role in the development of the final product microstructure.

Crystallization times may be several orders of magnitude lower for sheared melts than those required under quiescent conditions. This was measured for a wide variety of polymers (PE⁸⁻¹⁰, PB-1^{11,12}, PEO^{13,14}, PP⁹, ...). It is generally observed that the application of shear stress to initially supercooled melts leads to a decrease of the induction period and to a large increase in the number of crystalline structures^{8,9,12,15}. The effect of shear on the growth rate and on resulting morphology is not so clear, and is mainly function of the intensity of shear. Some authors have observed that oriented morphologies develop^{8,9} while other authors did not observed any significant change of the growth speed¹². It has also been observed that shear has a strong accelerating effect on crystallization when the strain rate exceeds a critical value⁹, but there is also a critical shear rate, depending on the molecular weight, beyond which a further increase of shear rate does not play a significant role¹³.

The importance of shear stress, rather than shear rate, is also demonstrated by the fast increasing effect of shear upon crystallization when supercooling and, hence, shear stress is increased^{15,16}. This can be explained by the competition between two effects, namely the orientation of the macromolecules due to the imposed shear, and on the other hand, the relaxation of this orientation due to the

natural thermal motion of the polymeric chains. The orientation process as well as the relaxation process are both affected by the viscosity. The shear stress, which is a function of shear rate and viscosity (rather than shear rate), appears to be the most important parameter affecting the shear induced crystallization process.

Isothermal crystallization kinetics of polymer have been extensively analysed with the aid of the well-known Avrami model. Application of this model to shear-induced crystallization kinetics has been attempted by several authors, but still remains much debated. Smith and Steward¹⁷ have studied the rate of crystallization of PET fibres, which is strongly dependent on the degree of orientation, but claimed that crystallization of oriented polymer cannot be described by the Avrami model. In order to model the effect of shear upon crystallization, Janeschitz-Kriegl and co-workers¹⁸⁻²¹ have developed a theoretical model of shear induced crystallization combining elements of polymer melt rheology and polymer crystallization. This model exhibits, at least qualitatively, all the features that can be expected for such a process.

However, Gupta and Auyeung²², who studied the crystallization kinetics of oriented PET with the Avrami model, have however noticed that the crystallization rate can be correlated at each temperature with the instantaneous value of the polymer chain orientation factor in the amorphous region. Sherwood *et al.*¹⁶ also describe the crystallization kinetics of PEO and PCL under shear by using this model. They observe an increase of the Avrami coefficient from 3 to 6, whereas the kinetic parameter undergoes a non negligible decrease (from 2 to 3 orders of magnitude). Monasse and Fryda²³ have described the shear-induced crystallization of PE with an empirical extension of the Avrami model. Kim and Kim²⁴ have studied the crystallization of preliminarily sheared samples by means of a capillary rheometer. They have shown that the shear history of a PET resin leads to a memory effect, which in turn affects the crystallization kinetics. Their results were analysed by means of a modified Avrami equation. The controversy about the Avrami model for representing shear-induced crystallization is mainly due to its geometrical assumption of sphere-, disc- or rod-shaped spherulites, while oblong spherulites and even *shish-kebab* structures are experimentally observed.

The purpose of the present work is to develop an appropriate crystallization model, able to accurately predict the crystallization kinetics of sheared PET melts.

2. Modelling

2.1. The consecutive Avrami model

In a previous work²⁵⁻²⁷, isothermal and non-isothermal crystallization kinetics of PET have been analysed and a suitable polymer crystallization model, the *consecutive Avrami model*, was developed. This model, which is an extension of the Avrami model²⁸, takes into account three major phenomena observed in quiescent crystallization, namely the induction time, the final degree of crystallinity and the secondary crystallization (which is consecutive to the first mechanism). In the case of isothermal conditions, the model is written in the form :

$$\alpha_v^c(t) = \frac{\alpha_v(t)}{\alpha_v^\infty} = w_1 \left(1 - \exp(-k_1 (t - t_0^1)^{n_1}) \right) + (1 - w_1) \left(1 - \exp(-k_2 (t - t_0^2)^{n_2}) \right) \quad , \quad (1)$$

where α_v^c is the relative crystallinity degree while $\alpha_v(t)$ is the real degree of crystallinity, both being functions of time (t); t_0^1 and t_0^2 , k_1 and k_2 , n_1 and n_2 are the induction time, the kinetic parameter and the Avrami coefficient for primary and secondary crystallization, respectively; w_1 is the relative weight fraction of the primary mechanism contribution and α_v^∞ is the ultimate degree of crystallinity in the sample at the end the crystallization experiment. As each of these parameters, except the Avrami coefficients, depends on temperature, interpolation functions must be determined in order to complete the model.

It is essential to clearly understand the meaning of the induction time of the primary mechanism nucleation rate. Nuclei are assumed to pre-exist in the melt. The number of these hypothetical nuclei is a function of time, temperature, shear and possibly pressure. The induction time is assumed to be the time that is required by the macromolecules to arrange themselves in order to activate the nuclei. The activation of these nuclei is therefore effective only when the induction time elapsed.

This model has been adapted to non-isothermal crystallization by using the approach of Nakamura *et al.*²⁹, which is based on the following assumption: the rate of crystallization at time t only depends on the temperature and the degree of crystallinity reached at that time, independently of the crystallization history. The non-isothermal model is thus written as :

$$\begin{aligned} \alpha_v(t) = & \int_0^t \alpha_v^\infty w_1 \frac{\partial}{\partial \tau} \left(1 - \exp \left(- \left[\int_{t_0^*}^\tau \sqrt[n_1]{k_1} ds \right]^{n_1} \right) \right) d\tau \\ & + \int_0^t \alpha_v^\infty (1-w_1) \frac{\partial}{\partial \tau} \left(1 - \exp \left(- \left[\int_{t_0^*}^\tau \sqrt[n_2]{k_2} ds \right]^{n_2} \right) \right) d\tau . \end{aligned} \quad (2)$$

To perform this transformation, the Avrami coefficients must be kept constant, while the thermal dependence of every other parameter must be known in the whole range of temperature $[T_g, T_m^0]$. We compute the non-isothermal induction time by the method suggested by Sifleet *et al.*³⁰, who define an accumulated induction time factor (θ_i) :

$$\theta_i = \int_0^{t_0^*} \frac{1}{t_0^i} dt . \quad (3)$$

When this accumulated induction time factor reaches 1.0, induction is assumed to be complete and the crystallization process « i » begins.

In order to introduce this crystallization model into a numerical simulation software, a differential system of rate equations is preferred, which is however easily obtained :

$$\begin{cases} \frac{D\theta_i}{Dt} = \frac{1}{t_0^i} , \\ \frac{D\alpha_{vi}^c}{Dt} = n_i k_i^{1/n_i} (1 - \alpha_{vi}^c) (-\ln(1 - \alpha_{vi}^c))^{1-1/n_i} , & \text{if } \theta_i \geq 1 , \\ \quad \quad \quad = 0 , & \text{if } \theta_i < 1 , \\ \frac{D\alpha_v}{Dt} = \alpha_v^\infty \left(w_1 \frac{D\alpha_{v1}^c}{Dt} + (1-w_1) \frac{D\alpha_{v2}^c}{Dt} \right) . \end{cases} \quad (4)$$

This very useful model accurately predicts the crystallization behaviour of PET in a DSC apparatus under both isothermal and non-isothermal conditions²⁷.

2.2. Why a new model ?

The Avrami model is based on a single kinetic parameter, which is a function of both; on the one hand, the nucleation rate (in case of homogeneous nucleation) or the number of nuclei (in case of heterogeneous nucleation) and, on the other hand, the growth rate of the crystalline entities. In the case of instantaneous nucleation and spherical growth, the kinetic parameter k is written in the form :

$$k = \frac{4}{3}\pi N G^3, \quad (5)$$

where N and G are the number of nuclei and the growth rate, respectively.

However, in the case of shear induced crystallization, a coupling between the nucleation rate (or the number of nuclei) and the growth rate can no longer be assumed when the shear applied to the sample varies with time. Consider indeed a polymer for which the nuclei generation is highly sensitive to the applied shear, and which experiences an isothermal crystallization in two steps. In the first step, a high shear is applied, which results in the apparition of an important number of nuclei. Next, in the second step, the sample returns to rest. At this time, the number of nuclei does not decrease as long as the sample temperature remains below its melting point (T_m). However, in Eq. (5), the number of nuclei (N), which is a function of present temperature and shear only, will become $N(T, \sigma = 0)$. The kinetic parameter will then immediately decrease to the no shear value.

This simple example illustrates the inability of the Avrami model to correctly represent crystallization when the shear history experienced by the sample must be taken into account. The *consecutive Avrami model*, which is an extension of the Avrami model, therefore reveals to be inadequate when complex thermomechanical histories, as encountered in polymer processing, must be taken into account.

2.3. A system of rate equation

A new model is proposed in this thesis, which combines the model of Schneider *et al.*^{31,32} with our *consecutive Avrami model*. The approach of Schneider *et al.*, on the one hand, was developed for one crystallization mechanism only, and defines a set of four differential equations governing, for each material point, the

evolution of the fictive crystallization distribution. On the other hand, the relation between effective and fictive relative crystallinity degrees is provided by the Avrami postulate. In order to understand the major importance of the approach proposed by Schneider *et al.*, it will first be presented in detail.

Let us define the expression $v_s(\vec{x}, t, \tau)$ as the volume at time t of a crystalline spherulite that has appeared in a given location $\vec{x}$, at the time $\tau < t$:

$$v_s(\vec{x}, t, \tau) = \frac{4}{3}\pi \left(\int_{\tau}^t G(\vec{x}, s) ds \right)^3, \quad (6)$$

where $G \geq 0$ is the radial growth speed of spherulites. The fictive crystalline volume fraction $\alpha_f(\vec{x}, t)$ is therefore the sum of the volume contributions, at time t , of all the spherulites that have been formed over the time interval $[0, t]$, namely:

$$\alpha_f(\vec{x}, t) = \int_0^t \dot{N}(\vec{x}, \tau) v_s(\vec{x}, t, \tau) d\tau, \quad (7)$$

where $\dot{N}(\vec{x}, \tau)$ is the nucleation rate per unit of volume, i.e. the number of new crystals appearing per unit of volume and time at the position $\vec{x}$ and time τ , including the phantom nuclei that appear within the previously crystallized fraction. Usually, for instantaneous nucleation and under constant crystallization condition, Eq. (7) reduces to:

$$\alpha_f(\vec{x}, t) = k(\vec{x}, t) t^3. \quad (8)$$

The mathematical model of Schneider *et al.* is build up as follows. Differentiating Eq. (7) with respect to time, one gets the crystallization kinetic equation:

$$\frac{D\alpha_f(\vec{x}, t)}{Dt} = 4\pi G(\vec{x}, t) \int_0^t \dot{N}(\vec{x}, \tau) \left(\int_{\tau}^t G(\vec{x}, s) ds \right)^2 d\tau. \quad (9)$$

This integro-differential equation is difficult to handle and it is more convenient to introduce a system of rate equations. To this end, letting the constants ω_i stand for $\omega_0 = 1$, $\omega_1 = 2$, $\omega_2 = \pi$ and $\omega_3 = \frac{4}{3}\pi$, 4 successive functions $g_i(\vec{x}, t)$ are defined as follows:

$$g_i(\vec{x}, t) = \omega_i \int_0^t \dot{N}(\vec{x}, \tau) \left(\int_{\tau}^t G(\vec{x}, s) ds \right)^i d\tau \quad (i = 0, 1, 2, 3). \quad (10)$$

Note that $g_3(\vec{x}, t) = \alpha_f(\vec{x}, t)$, and that $g_0(x, t)$ is the total number, per unit volume, of fictive spherulites that have appeared, at the position $\vec{x}$, up to the time t . Moreover $g_1/2g_0$ and $4g_2/g_0$ are the averages at time t of the radii and the areas of the fictive spherulites, respectively. The functions g_i satisfy the following system of differential equations :

$$\begin{cases} \frac{Dg_0}{Dt} = \dot{N} , \\ \frac{Dg_i}{Dt} = \left(\frac{\omega_i}{\omega_i - 1} \right) i G g_{i-1} , \quad (i = 1, 2, 3) , \end{cases} \quad (11)$$

with $g_i(\vec{x}, t) = 0$ as initial conditions.

The approach of Schneider *et al.* allows one to separately model the nucleation and growth processes in the case of spherulitic crystallization. The beauty of this theory lies in the fact that the time derivative of the volume of the fictive spherulites is exactly the product of their total surface by the growth rate, while the time derivative of this latter surface is the product of the total diameter of the fictive spherulites by the growth rate, and the time derivative of this total diameter is itself the product of the number of fictive nuclei by the growth rate. Hence, only two kinetic parameters – the growth rate (G) and the nucleation rate ($\dot{N}$) – must be determined experimentally to complete the model.

2.4. Towards a new crystallization model

Compared to the *consecutive Avrami model*, the model of Schneider *et al.* does not take into account other physical phenomena such as nucleation induction time, spherulites impingement, secondary crystallization and the presence of an ultimate degree of crystallinity. It will however permit us to accurately take into account the impact of shear on the nucleation process since no assumption has been formulated concerning this process. It can be either homogeneous or heterogeneous, influenced by complex temperature and shear histories. However, the main restriction of this model concerns the spherulitic growth assumption. Spherulites (as in the Avrami model) can either be rods ($i = 1$), discs ($i = 2$) or spheres ($i = 3$). This assumption is excessive in the case of shear-induced crystallization when oblong or *shish-kebab* like

crystalline entities are observed. A generalization of this model to non-isotropic geometries is however beyond the scope of the present study.

The approach of Schneider *et al.* is however very useful, since it allows us to strongly improve the *consecutive Avrami model*. Indeed, the equation describing the primary mechanism of crystallization in Eq. (4) can be replaced by the system of rate equations (11), where the fictive crystallization distribution is characterised by four state variables, namely, the number of fictive nuclei per unit volume N_1 , and the sums of their diameters R_1 , outer surfaces S_1 and volumes V_1 , respectively (again per unit volume). As the fictive crystalline volume, per unit volume of polymer, is also the fictive crystallinity degree of the melt (α_f), the Avrami postulate has allowed us to determine the effective relative crystallinity (α_{v1}^c) from the fictive degree by the differential law :

$$\frac{D \alpha_{v1}^c}{D t} = (1 - \alpha_{v1}^c) \frac{D \alpha_f}{D t} \quad (12)$$

The new global system of equation can therefore be written in the following form :

$$\left\{ \begin{array}{l} \frac{D \theta_1}{D t} = \frac{1}{t_0^1} \\ \frac{D N_1}{D t} = \dot{N} \\ \frac{D R_1}{D t} = 2 G N_1 \quad \text{if } \theta_1 \geq 1 \quad \text{else} \quad \frac{D R_1}{D t} = 0 \\ \frac{D S_1}{D t} = \pi G R_1 \\ \frac{D V_1}{D t} = 4 G S_1 = \frac{D \alpha_f}{D t} \\ \frac{D \alpha_{v1}^c}{D t} = (1 - \alpha_{v1}^c) \frac{D \alpha_f}{D t} \\ \frac{D \theta_2}{D t} = \frac{1}{t_0^2} \\ \frac{D \alpha_{v2}^c}{D t} = n_2 k_2^{1/n_2} (1 - \alpha_{v2}^c) (-\ln(1 - \alpha_{v2}^c))^{1-1/n_2} \quad \text{if } \theta_2 \geq 1 \quad \text{else} \quad \frac{D \alpha_{v2}^c}{D t} = 0 \\ \frac{D \alpha_v}{D t} = \alpha_v^\infty \left(w_1 \frac{D \alpha_{v1}^c}{D t} + (1 - w_1) \frac{D \alpha_{v2}^c}{D t} \right) \end{array} \right. \quad (13)$$

In this system of rate equations, the approach of Schneider *et al.* was not used for modelling the secondary crystallization mechanism, as long as distinct data for the nucleation rate and the growth rate cannot be experimentally obtained for this process and that its physical behaviour is completely different. It is interesting to note that, when no shear, or when a constant shear (having a constant effect on the whole process), is applied, the new model reduces to the differential form of the *consecutive Avrami model* (Eq. (4)).

2.5. Remark concerning the nucleation rate

According to Eder *et al.*³³ the most general law for nucleation rate, if an activation time distribution is assumed, is :

$$\dot{N} = \sum_i \frac{N_i}{\tau_i} \exp\left(-\int_{-\infty}^t \frac{ds}{\tau_i}\right) \quad , \quad (14)$$

where N_i is the number of potential sites per unit volume for the nucleation process « i » and τ_i is the corresponding activation time as a function of temperature and shear. This equation, however, contains too many parameters, which could never be determined by experiments. In order to simplify this relation, the assumption is made, as suggested by Janeschitz-Kriegl *et al.*³⁴, that the activation times of all processes, which are certainly infinite at the equilibrium melting point, remain infinite during cooling until their peculiar induction time is reached. At that time, the corresponding activation time τ_i is assumed to jump to zero. In this way, one obtains for the total number of activated sites per unit volume the relation :

$$N(t) = \sum_i N_i \quad \text{with } t > t_0(i) \quad . \quad (15)$$

In this way, not only G is obtained as a function of temperature, shear and pressure but also N as such a function. Formally, one also obtains the expression of $\dot{N}$:

$$\dot{N} = \frac{D N(t)}{Dt} \quad , \quad (16)$$

as the rate of activation. Hence, in the case of a complex thermomechanical history, Eq. (16) is transformed into the following set of equations :

$$\begin{cases} \dot{N} = \frac{\partial N}{\partial T} \frac{DT}{Dt} \Big|_{\text{if } \frac{\partial N}{\partial T} \frac{DT}{Dt} > 0} + \frac{\partial N}{\partial \sigma} \frac{D\sigma}{Dt} \Big|_{\text{if } \frac{\partial N}{\partial \sigma} \frac{D\sigma}{Dt} > 0} & \text{if } T < T_m \\ N = N(T, \sigma) & \text{if } T > T_m \end{cases} \quad (17)$$

taking into account the fact that, below T_m , the number of nuclei never decreases.

3. Experimental

The PET grade used for the present investigation, namely PET A02-304 (Mn $\approx$ 20000), was supplied by DSM. In polycondensates, moisture has a great influence on crystallization, since it reduces molecular mass by hydrolysis and thus increases the nucleation rate. The samples were held 8 hours at 120°C under vacuum, in order to remove the absorbed moisture. To avoid thermal degradation of the polymer, a new sample had to be used for each thermal cycle, and experiments were carried out under a nitrogen atmosphere.

Quiescent crystallization kinetics of PET have been carried out using a Perkin-Elmer DSC2B. The experimental procedure for measuring experimental kinetics by DSC has been previously detailed in Chapter II.

Shear induced crystallization was studied through viscosity measurements carried out with a high temperature CARIMED cone and plate rheometer (CSL 500). A set of 10 mm diameter disc samples were cut from a pre-pressed PET sheet of about 1 mm thickness. In general, an accurate control of the experimental conditions shows to be very important in order to ensure the reproducibility and accuracy of the measurements. Here, the key parameters are the temperature during the whole cycle (which consists of complete melting, cooling at the crystallization temperature and isothermal or non isothermal control during the experiment) and the adjustment of the gap to take the volume changes of the sample into account. Unfortunately, some experimental dispersion cannot be avoided due to the non-homogeneity of the samples, the slight variation of the gap thickness during the experiments when crystallization starts, and the thermal expansion of the experimental set-up. Moreover, viscous dissipation and release of crystallization heat in the sample during

the experiment, which can have important effects³⁶, were neglected in the present study.

Isothermal shear induced crystallization experiments were performed from the melt, at 3 different temperatures (508, 513 and 518 K), and at a constant imposed shear stress ranging from 100 to 18000 Pa. Before recording the viscosity, the samples were heated up to 553 K and held at that temperature for 3 min. in order to ensure a complete melting of the polymer. They were afterwards rapidly cooled (at 40 K/min) to the constant imposed temperature. The temperature range is however limited at both ends. On the one hand, below 508 K, crystallization is too fast and the effect of shear-induced crystallization on viscosity cannot be observed. Moreover, in that case a cooling rate of 40K/min is not fast enough, since the sample starts to crystallize before the isothermal condition is reached. On the other hand, above 518 K, crystallization becomes too slow and degradation occurs.

The same melting history was used for non-isothermal experiments and cooling rates up to 20 K/min were imposed with constant imposed shear stress ranging from 200 to 8000 Pa.

The melt viscosity of the sample was measured, in the range of 533 to 583 K, at low and high shear rates with the cone and plate rheometer and a Göttfert 2002 capillary rheometer, respectively.

The final degree of crystallinity was measured in the sample after each crystallization experiment, with the aid of a Davenport gradient density column filled with successive concentrations of dissolved NaBr in water.

4. Computational procedure

In order to calculate the shear-induced crystallization kinetics from viscosity curves, the relation between the viscosity η_0 and the relative crystallinity of the sample (α_c^r) must be determined.

As the sample can be considered as formed by crystalline entities dipped into a melt, we can relate the increase of viscosity induced by crystallization to the

increase of viscosity of a suspension of growing spheres in a fluid. This latter system has been widely studied in the past, and several relations between the volume fraction of the spheres in the fluid and the viscosity of the system have been proposed :

$$\eta_0 = \eta_0^m \exp\left(\frac{2.5 \Phi}{1 - A \Phi}\right) \quad (\text{Mooney}) , \quad (18)$$

$$\eta_0 = \eta_0^m \frac{1}{(1 - \Phi)^{5/2}} \quad (\text{Brinkman}) , \quad (19)$$

$$\eta_0 = \eta_0^m \frac{1}{(1 - \Phi/A)^2} \quad (\text{Maron and Pierce}) , \quad (20)$$

$$\eta_0 = \eta_0^m (1 + A \Phi) \quad (\text{Einstein}) . \quad (21)$$

In these expressions, η_0 is the viscosity of the sample, η_0^m is the viscosity of the fluid, Φ is the volume fraction of the spheres and A is a parameter. The analogy between this system and the growth of crystalline entities in a melt allows to replace η_0^m by the viscosity of the melt and Φ by the relative degree of crystallinity α_v^c . However, from a theoretical point of view, the above relations are valid in dilute solutions only, which is not the case at the end of crystallization. Moreover, it is assumed that there is no interaction between the spheres and the solvent. In a polymer melt, the increase of viscosity will be faster than in such a system, due to the fact that each crystalline entity will play the role of a physical crosslink. Nevertheless, the sought relation can be assumed to be of the following form :

$$\eta_0 = \eta_0^m f(\alpha_v^c) . \quad (22)$$

The best method to obtain this relation would be to measure the evolution of the viscosity of a sample during a quiescent crystallization $\eta(t, \sigma=0)$, which is obviously impossible. An interesting method to bypass this problem is to perform a set of experiments at several imposed shear stresses and extrapolate the resulting curves to zero shear stress. This is possible because a critical shear stress is needed to observe an accelerating effect on crystallization. The ratio between the viscosity curve $\eta(t, \sigma=0)$ of the sample and the viscosity of the melt η_0^m gives the function $f(\alpha_v^c)$.

Assuming that Eq. (22), which is valid for quiescent crystallization, is still valid for shear-induced crystallization in the range of considered shear stresses, it is possible to calculate the crystallization kinetics corresponding to shear-induced crystallization experiments performed with the cone-plate rheometer. As the *consecutive Avrami model* is still valid under constant crystallization conditions, it is easy to determine the parameters of the model, thanks to the Levenberg and Marquard non-linear multivariable regression method³⁶, from both DSC and constant shear stress cone and plate isothermal experiments.

5. Results and discussion

5.1. Melt viscosity

Combined PET shear viscosity results obtained by means of the cone-plate and the capillary rheometer are represented on Fig. III.1 for several temperatures.

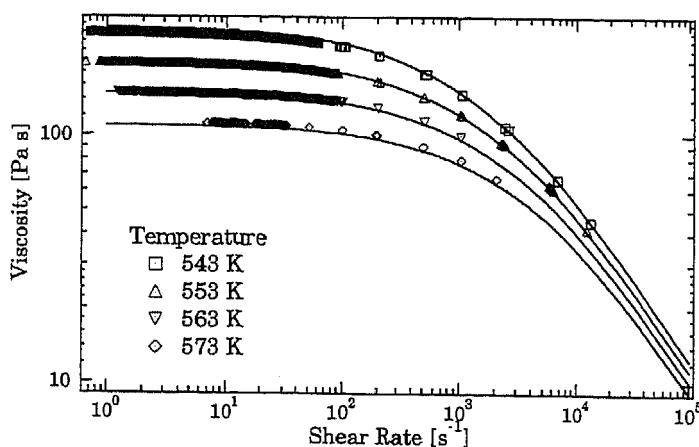


Figure III.1 : Viscosity of PET as a function of shear rate for several temperatures (log-log diagram).

These curves are characterized by a Newtonian plateau followed by a shear-thinning region, which behaviour is easily fitted by a Cross viscosity law :

$$\eta = \frac{\eta_0}{1 + \left(\frac{\eta_0 \dot{\gamma}}{\tau_0} \right)^{1-n}} \quad , \quad (23)$$

where $\dot{\gamma}$ is the shear rate, $\eta_0 = \eta_0^n f(\alpha_v^c)$ is the viscosity at low shear rate (Newtonian plateau), τ_0 is a material constant and n is the power index. The Newtonian melt viscosity η_0^n has been approximated by a modified Arrhenius law :

$$\eta_0^n = 9.7915 \cdot 10^5 \exp(-0.03032 (T-273)) [Pa] \quad , \quad (24)$$

while $\tau_0 = 3.616 \cdot 10^5 [Pa]$ and $n = 0.29635$.

5.2. Effect of shear induced crystallization on viscosity

Three sets of viscosity curves, for PET samples cooled from the melt to 508, 513 and 518 K, respectively, and submitted to different imposed shear stress, are reported in Fig. III.2. A sharp increase of viscosity (of about 2 orders of magnitude), resulting from the development of crystallinity, is observed. The expected acceleration of crystallization when the imposed shear stress increases is clear. In particular, the onset of the viscosity steep increase, which is representative of the crystallization induction time, is considerably reduced when shear stress increases. It is also observed that the effect of the imposed shear stress becomes more pronounced when the crystallization temperature increases.

Similar viscosity curves are reported in Fig. III.3 for a set of non-isothermal experiments. In this case also, an increase of the imposed shear stress accelerates the crystallization. However, when the cooling rate becomes too important, thermal effects become dominant, since crystallization starts at a lower temperature, while shear stress shows no significant effect on crystallization. From these results, one may suggest that the effect of shear stress on the crystallization behaviour of this polymer is not very important, especially when a high cooling rate is expected.

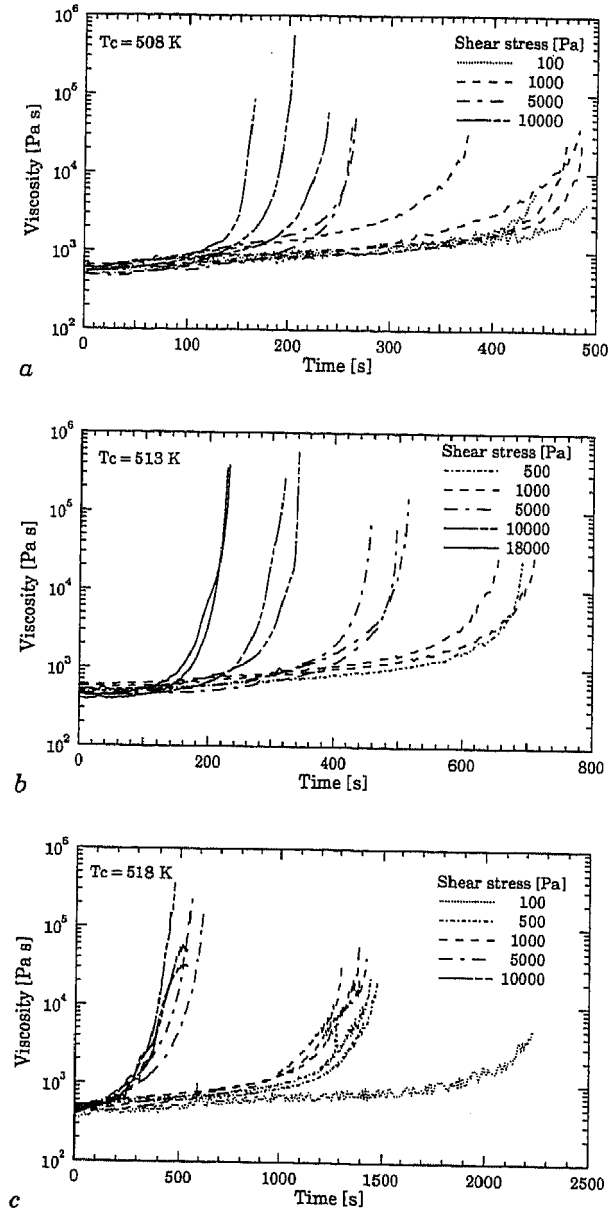


Figure III.2 : Time evolution of PET viscosity during isothermal shear-induced crystallization at constant imposed shear stresses (100 Pa (—), 500 Pa (---), 1000 Pa (---), 5000 Pa (—), 10000 Pa (—), 18000 Pa (—)), for three different temperatures (a, 508 K; b, 513 K; c, 518 K).

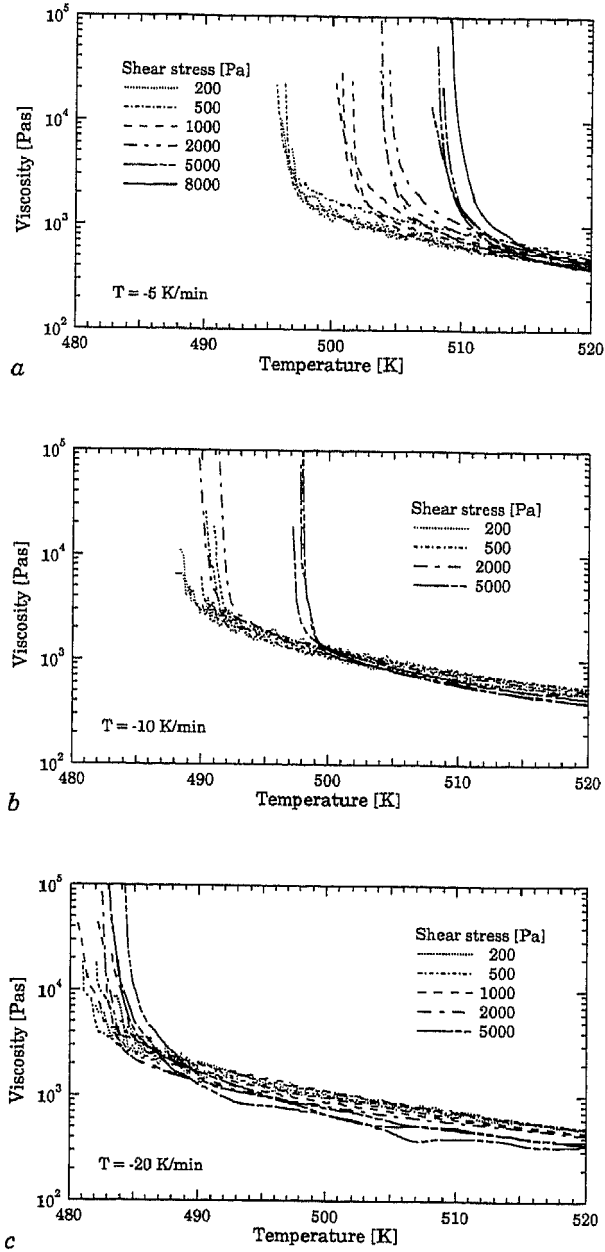


Figure III.3 : Evolution of PET viscosity as a function of temperature during non-isothermal shear-induced crystallization experiments performed at constant imposed shear stresses (200 Pa (— · — · —), 500 Pa (— · — · — · —), 1000 Pa (— · — · — · — · —), 2000 Pa (— · — · — · — · — · —), 5000 Pa (— · — · — · — · — · — · —), 8000 Pa (— · — · — · — · — · — · — · —)), for three different cooling rates (a, -5 K/min; b, -10 K/min; c, -20 K/min).

5.3. Relation between viscosity and relative degree of crystallinity

The function $f(\alpha_v^c)$ which expresses the increase of viscosity due to crystallinity, has been calculated from viscosity curves obtained by means of non-isothermal shear-induced crystallization experiments performed at the lowest imposed shear stress, thanks to Eqs. (22-24). This function (which is only time dependent) can be compared to corresponding quiescent non-isothermal crystallization kinetics numerically determined by means of the *consecutive Avrami model*. Fig. III.4 represents $f(\alpha_v^c)$ (i.e. the ratio between the sample viscosity and the melt viscosity) as a function of the relative crystallinity degree in the sample. This function starts from 1, when no crystallinity is present, and increases with the degree of crystallinity. Due to experimental limitations, viscosities higher than 50 times the melt viscosity cannot be reached. The relation is therefore limited to the presence of a very little crystallinity degree in the sample. Already for a crystallinity degree of 2-3 %, the viscosity is 10 times higher than that of a completely melted sample. Therefore, one observes that only a low degree of crystallinity is needed to solidify the sample.

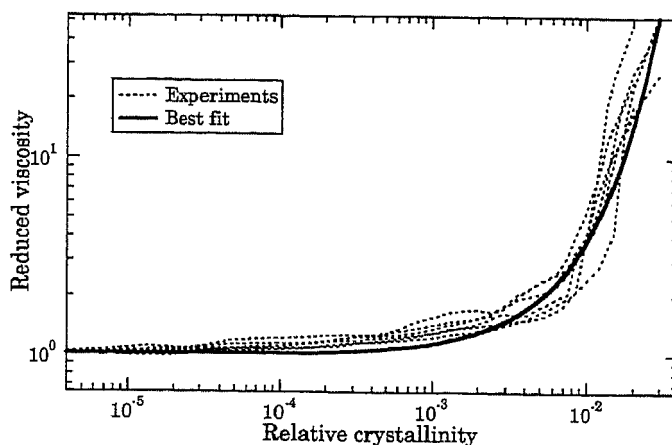


Figure III.4 Experimental relation between viscosity and relative crystallinity degree in a PET sample.

This result is in agreement with recent work by Titomanlio and Brucato³⁷, who performed experiments of flow induced crystallization of an isotactic polypropylene and concluded that the crystallinity degree that is required to significantly increase the viscosity is of the order of 2%. Such a result agrees with the picture that crystalline nuclei would act in the melt as physical crosslinks.

As suggested by theoretical considerations about the viscosity of a suspension of spheres in a solvent, the following relation was used for the fit :

$$\frac{\eta_0}{\eta_0^m} = \exp\left(\frac{a \alpha_v^c}{1 - b \alpha_v^c}\right) , \text{ if } b \alpha_v^c < 1 , \quad (25)$$

$$\frac{\eta_0}{\eta_0^m} = f_{\max} \quad \text{otherwise} .$$

We have imposed $f_{\max} = 1000$ and the thickest curve on the figure was obtained with $a = 104.1$ and $b = 18.618$.

5.4. Determination of the parameters of the crystallization model

5.4.1. Isothermal quiescent crystallization

The isothermal crystallization behaviour of PET has been analysed in Chapter II, and the temperature dependence of the parameters of the *consecutive Avrami model* has been determined. The assumption was made that primary crystallization of this PET proceeds by instantaneous nucleation and spherical growth. The relations obtained in Chapter II are here summarized :

– final degree of crystallinity α_v^∞ :

$$\alpha_v^\infty = (T - T_g) \left(\frac{100}{T_m^0 - T_g} + 2.622 \cdot 10^{-2} (T_m^0 - T) - 2.602 \cdot 10^{-5} (T_m^{02} - T^2) \right) ; \quad (26)$$

– weight w_1 :

$$w_1 = 1 - 4.737 \exp\left(-\frac{113.73}{T - T_g}\right) \cdot \exp\left(-\frac{162.51}{T_m^0 - T}\right) ; \quad (27)$$

– induction times t_0^1 and t_0^2 :

$$t_0^1 = 2.480 \cdot 10^{-3} \exp\left(\frac{299.7}{T - T_g}\right) \exp\left(\frac{472.37}{T_m^0 - T}\right) , \quad (28)$$

$$t_0^2 = 1.295 \cdot 10^{-1} \exp\left(\frac{209.7}{T - T_g}\right) \exp\left(\frac{405.6}{T_m^0 - T}\right) ; \quad (29)$$

- kinetic parameters k_1 and k_2 :

$$k_1 = 8.466 \cdot 10^7 \exp\left(-\frac{1.201 \cdot 10^3}{T - T_g + 24}\right) \exp\left(-\frac{4.601 \cdot 10^8}{T^2(T_m^0 - T)}\right) , \quad (30)$$

$$k_2 = 1.688 \exp\left(-\frac{2.293 \cdot 10^2}{T - T_g + 24}\right) \exp\left(-\frac{7.159 \cdot 10^7}{T^2(T_m^0 - T)}\right) ; \quad (31)$$

- Avrami coefficients n_1 and n_2 : imposed equal to 3 and 1, respectively.

In order to use the improved crystallization model developed in the present work, the kinetic parameter of the primary crystallization mechanism k_1 must be replaced, as unknown parameter, by the number of nuclei N and the growth rate G . However, the accurate determination of the thermal and shear dependency of these two parameters was not experimentally possible in the scope of this study. An approximate method was therefore used. On the one hand, as already mentioned, primary crystallization is assumed to proceed by an instantaneous nucleation of the spherulites. The parameter k_1 is thus defined, in agreement with the Avrami theory, by the following relation :

$$k_1 = \frac{4}{3} \pi N G^3 . \quad (32)$$

On the other hand, Van Krevelen³⁸ has determined the number of nuclei that are present after crystallization from the melt for different polymers, including PET. A unique thermal dependency was found, which can be modelled by the following equation :

$$N = 10^9 \exp\left(\frac{7.5 (T_m - T) + 5 (T - T_g)}{T_m - T_g}\right) \quad [\# / m^3] . \quad (33)$$

Using Eqs. (30), (32) and (33), it is therefore possible to compute the thermal dependence of G , which has been fitted to give the following relation :

$$G = 10^{-9} \exp\left(14.42 - \frac{413.3}{T - (T_g - 24)} - \frac{435.7 T_m^2}{T^2 (T_m - T)}\right) \quad [m/s] . \quad (34)$$

The so-calculated thermal dependence of growth rate is close to the experimental measurements performed by Van Antwerpen³⁹, as shown in Fig. III.5. This

demonstrates the relative exactness of our approach. This method also ensures to retrieve the predetermined parameter k_1 when crystallization occurs with no shear.

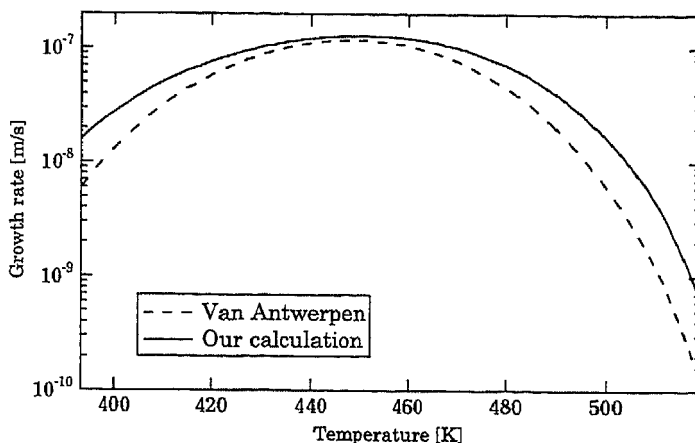


Figure III.5 Growth rate of PET as a function of temperature. Comparison between the growth rate dependence obtained by Van Antwerpen and the results obtained from Eqs. (30), (32) and (33).

5.4.2. Isothermal shear induced crystallization.

For isothermal kinetics at constant imposed shear stress, the *consecutive Avrami model* remains valid, and shear stress can be introduced as a variable in the model governing parameters. It is known that induction time and nucleation rate (or nuclei number) are essentially affected by shear, while no significant effect is observed upon the growth rate as long as the shear stress remains below some given critical value. Shear can also have an impact on the final degree of crystallinity. However, in the present study, the Avrami coefficients have been assumed to keep their quiescent crystallization value because the new model, as well as the *consecutive Avrami model*, are not able to describe the growth of other entities than spheres (or discs or rods).

Thanks to Eq. (25), viscosity curves obtained from the rheometer, during isothermal shear-induced crystallization experiments, can be transformed into shear-induced crystallization kinetics. Fig. III.6 represents the crystallization kinetics of PET at 513 K for 5 imposed shear stresses. As it has already been observed, the

viscosity increases drastically when crystallization starts, and the kinetics can be measured during the beginning of the process only (corresponding to a maximum of 5% in term of relative crystallinity degree). For such a low crystallinity, it can be assumed that only the first crystallization mechanism is active. Only the shear dependence of the parameters of the first mechanism can therefore be determined, while the values of the other parameters (i.e. the relative weight of the primary mechanism and the parameters of the secondary mechanism) have been kept equal to the values obtained for the pure thermal model.

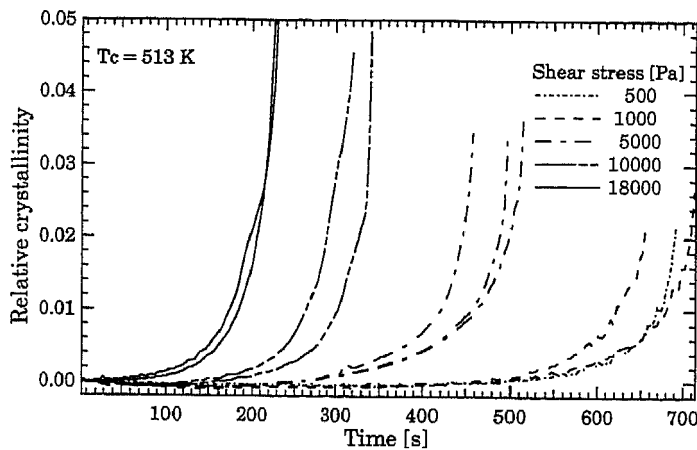


Figure III.6 : Isothermal shear-induced crystallization kinetics of PET for 5 imposed shear stresses.

Fig. III.7 shows the final degree of crystallinity in the sample after each isothermal rheometer experiments. No effect of shear stress on this parameter is observed.

In order to develop our model in a wide range of temperature, we have assumed that the effects of temperature and shear stress on the induction time and the kinetic parameter can be decoupled :

$$t_0^1(T, \sigma) = t_0^1(T) t_0^{1''}(\sigma) \quad , \quad (35)$$

$$k_1(T, \sigma) = k_1(T) k_1''(\sigma) \quad . \quad (36)$$

In these formulas, the factors $t_0^i(T)$ and $k_1^i(T)$, can be independently determined from DSC experiments (Eqs. (28) and (30)), while the factors $t_0^i(\sigma)$ and $k_1^i(\sigma)$ are defined as the reduced induction time and the reduced kinetic parameter. Thanks to Eqs. (35) and (36), the shear stress dependence of these reduced parameters (shown in Figs. III.8 and III.9) is easily determined by fitting experimental isothermal shear-induced crystallization kinetics by the *consecutive Avrami model*.

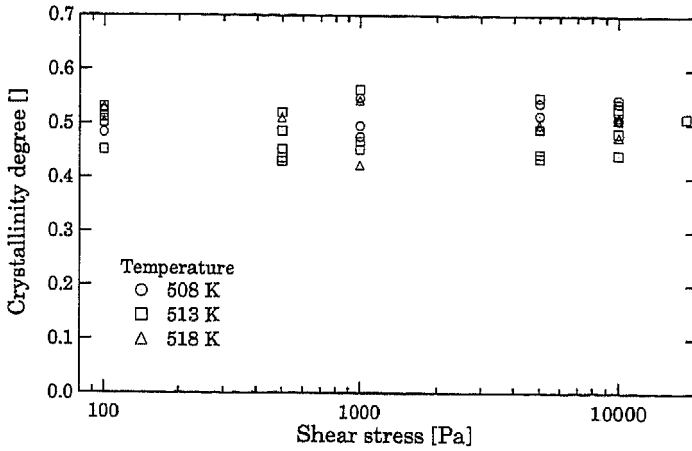


Figure III.7 : Degree of crystallinity in a PET sample as a function of imposed shear stress, after 3 sets of isothermal shear-induced crystallization experiments : (at 508 K, 513 K and 518 K).

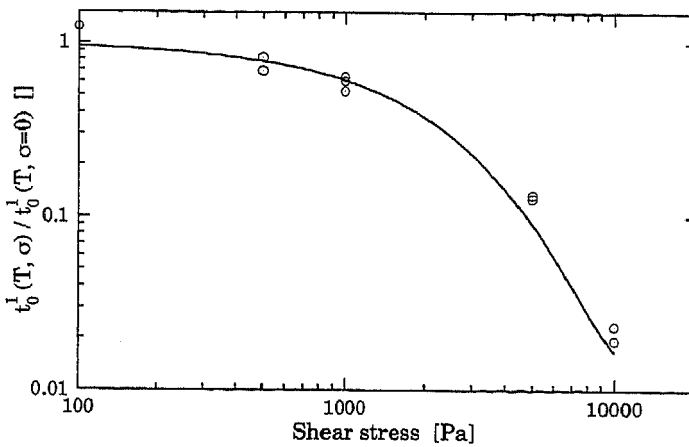


Figure III.8 : Reduced induction time as a function of imposed shear stress.

It should be observed that the induction time is reduced by 2 orders of magnitude when the shear stress increases; this decrease occurs mainly beyond 1000 Pa. The presence of a plateau at low shear was already observed by Lagasse and Maxwell⁹ on PE and PP. On the other hand, it is also observed that the reduced kinetic parameter continually increases with shear stress.

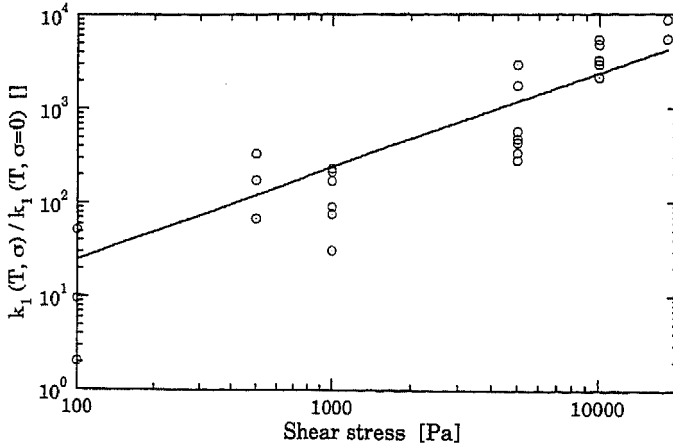


Figure III.9 : Reduced kinetic parameter as a function of imposed shear stress.

In order to insure that the thermal value of the parameters are obtained when no shear is applied, the interpolation functions of the reduced parameters must be equal to 1 when $\sigma = 0$, while an asymptotic plateau must in addition be exhibited at high shear stress. The following functions can be used :

$$t_0^*(\sigma) = a_t + (1 - a_t) \exp(-b_t \sigma) \quad \text{with } 0 < a_t < 1, \quad (37)$$

$$k_1^*(\sigma) = a_k + (1 - a_k) \exp(-b_k \sigma) \quad \text{with } a_k > 1, \quad (38)$$

giving the following values, after fit on the experimental points of Figs. III.8 and III.9 : $a_t = 0.01$; $b_t = 5.01 \cdot 10^{-4}$; $a_k = 9.49 \cdot 10^4$; $b_k = 2.51 \cdot 10^{-6}$.

The shear stress dependence of N and G can be determined by using the same principles as for the determination of their thermal dependence. Unfortunately, without any complementary experimental data, the splitting of $k_1^*(\sigma)$ into a pair of functions $N''(\sigma)$ and $G''(\sigma)$ is not possible. Nevertheless, with the assumption that

shear has an impact on the nucleation rate only, and because Eq. (32) is linear in N , the shear stress dependence of the number of nuclei is exactly the same as the dependence obtained for the kinetic parameter (Eq.(38)) :

$$N''(\sigma) = a_k + (1 - a_k) \exp(-b_k \sigma) \quad (39)$$

5.5. Validation of the model

The introduction of Eqs. (26-29, 31, 33-37 and 39) into the extended form of the *consecutive Avrami model* (Eq.(13)) allows to predict non-isothermal shear-induced crystallization kinetics. These predictions can further be transformed into viscosity curves by means of Eq. (25). In particular, Fig.III.10 represents the viscosity prediction for a shear-induced crystallization at -5K/min for several imposed shear stresses, as compared to corresponding experimental viscosity curves. The sharp increase of viscosity due to the onset of crystallization in the sample is correctly predicted. The prediction accuracy can be considered as being quite good, having in mind the experimental problems and the model limits.

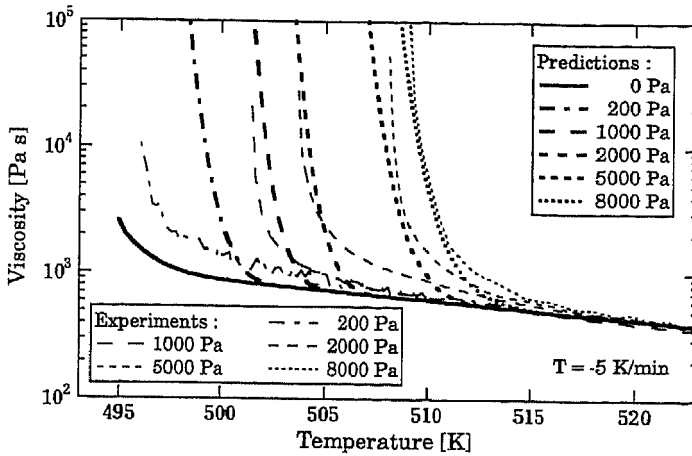


Figure III.10: PET viscosity as a function of temperature during non-isothermal shear-induced crystallization at -5 K/min for 5 constant imposed shear stresses. Comparison between experiments and model predictions.

6. Conclusions

In this study, we have proposed a new crystallization model, that is able to handle shear-induced crystallization when the polymer experiences a complex thermomechanical history. This new model combines most of the advantages of both our *consecutive Avrami model* and the approach of Schneider *et al.*³¹ It results in a set of differential equations that take induction time, final degree of crystallinity and the presence of secondary crystallization into account, and which separate the nucleation and growth processes in primary crystallization. The main limitation of the proposed model consists in the assumption of growth of spherical crystalline entities. The model must thus be further developed when highly oriented crystalline entities are present. Moreover, the concept of induction time should be clarified from a theoretical point of view.

Shear-induced crystallization of PET was studied by cone and plate rheometry, which has proved to be a powerful experimental set-up for such studies. As shear stress is a more suitable parameter than shear rate, a constant stress rheometer reveals to be more efficient than a constant shear rate rheometer. The main limitation of this equipment is the limit in sensitivity of the rotation speed sensor, which is quickly reached when the sample becomes solid. It could be very interesting to superpose a small oscillation on the imposed shear stress flow in order to obtain the dynamic viscosity of the sample during the whole experiment, because this latter property remains measurable when the sample becomes solid.

In order to obtain the shear induced crystallization kinetics, a relation between viscosity and crystallinity in the sample has been determined. It has been observed that a very low crystallinity degree in the sample (2-3%) is sufficient to hugely increase its viscosity.

On the basis of isothermal shear-induced experiments, the shear stress dependence of the parameters of the crystallization model have been evaluated. However, as experimental shear-induced crystallization kinetics were limited to very low crystallinity levels, only the effect of shear on the parameters of the primary crystallization mechanism has been determined. A decrease of the induction time

and an increase of the kinetic parameter (which can be interpreted as an increase of the generated number of nuclei) were observed when shear stress is increased. The effect of shear stress on the crystallization of the PET analysed in this study (DSM PET A02-304) was however found to be less important as it might be thought. Indeed, at a cooling rate of 20 K/min, the effect of stress is not so clear, while the effect of temperature remains predominant.

Finally, it should be stressed that the proposed model shows good agreement when compared to non-isothermal shear-induced crystallization experiments.

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Chapter IV

Injection Moulding Modelling

Abstract

A mathematical model describing the injection moulding process of thermoplastics is described. The "thin film approximation" is introduced to simplify the main balance and constitutive equations, thereby leading to a full set of equations governing the pressure, velocity and temperature fields (the well known so-called Hele-Shaw model). In a second step, the numerical method developed to solve these equations is summarized. Finally, the chapter ends with the description of a particle tracking algorithm, that allows for the reconstruction of the thermomechanical histories of injected material points.

1. Introduction

The filling stage of injection moulding is characterised by a time-dependent non-isothermal non-Newtonian flow with moving free surfaces. As for any industrial process, its mathematical description consists of balance and constitutive equations, completed with a proper set of boundary and initial conditions. These basic modelling questions are addressed in Section 2.

Major simplifying hypotheses must in addition be adopted at the outset in order to solve the problem, especially in view of the geometrical complexity of common industrial components. In Section 3, the simplifications commonly applied in injection moulding are described, with a special emphasis on the "thin film approximation" and the definition of the pressure and temperature problems. Most of the effects neglected when using these simplifications have minor consequences upon the flow behaviour, while the computation time is considerably reduced when approximate equations are introduced. This section ends with a system of equations (the so-called Hele Shaw model) which forms the basis of the simulation algorithm and describes the behaviour of the molten thermoplastic fluid during the filling and packing processes. Provided the geometry of the mould cavity, the material behaviour and the process operating parameters are known, these equations can, in principle, be solved. Results indicate the course of events that take place during the process.

In practice, however, the resulting system of partial differential equations can only be solved numerically, because of its complexity and non-linearity. The principles and procedures that are used in the injection moulding simulation software *MOLDSYS*¹ (in which our developments were included) are described in Section 4.

Finally, a tracking algorithm allowing for the reconstruction of the thermomechanical history of any selected injected material point is described in Section 5.

In each section, the impact of crystallization on the general model is considered with a particular attention.

2. Fundamental equations

In this section, the general balance equations are recalled and the constitutive equations of an injection moulded polymer are introduced. The section ends with a description of the proper set of boundary and initial conditions commonly used in injection moulding.

2.1. Balance equations

Balance equations, which are presented here in local form, are derived from the basic laws of continuum mechanics. For a more detailed description, the reader is referred to Bird *et al.*²

Balance of mass (continuity equation):

$$\frac{D\rho}{Dt} + \rho(\bar{\nabla} \cdot \vec{v}) = 0 \quad , \quad (1)$$

where ρ denotes the specific mass; t is the time; $\vec{v}$ is the velocity vector and $\bar{\nabla}$ stands for the gradient operator.

Balance of momentum:

$$\bar{\nabla} \cdot \boldsymbol{\sigma}^t + \rho \vec{f} = \rho \frac{D\vec{v}}{Dt} \quad , \quad (2)$$

where $\boldsymbol{\sigma}$ is the Cauchy stress tensor and $\vec{f}$ represents the specific body forces.

Balance of moment of momentum:

$$\boldsymbol{\sigma} = \boldsymbol{\sigma}^t \quad . \quad (3)$$

Balance of energy (first law of thermodynamics):

$$\rho \frac{De}{Dt} = \boldsymbol{\sigma} : \mathbf{D} - \bar{\nabla} \cdot \vec{q} + \rho r \quad , \quad (4)$$

where e is the specific internal energy; $\mathbf{D}$ is the rate of deformation tensor; $\vec{q}$ is the heat flux vector and r is an external specific heat source.

2.2. Constitutive equations

Balance equations can only be solved if specific relations are in addition given, that express ρ , α , $\bar{q}$ and e as functions of the past temperature and motion in the vicinity of each material point.

Cauchy stress tensor

Many different constitutive models exist that relate the Cauchy stress tensor to the independent variable ρ , and the temperature and deformation histories³. Since we are basically interested in the flow kinematics and its impact on polymer crystallization, only the generalized Newtonian model has been used. Indeed, this model is commonly employed in the simulation of the filling stage of injection moulding, since it can be shown that viscoelastic effects have a reduced influence on the velocity field during this stage⁴. The generalized Newtonian model was also used in this thesis for simulating the packing and cooling stages of the process. Let us however note that viscoelasticity should be taken into account when residual stresses or flow-induced stresses must be determined. For example, Douven⁴ has compared flow-induced stress predictions from the compressible Leonov and Wagner models, while Kabanemi and Crochet⁵ have used a linear thermo-viscoelastic model (using the concept of fictive temperature) for predicting thermal residual stresses.

The Cauchy stress tensor σ is generally split into a hydrostatic part $-p \mathbf{I}$ and an extra stress tensor τ :

$$\sigma = -p \mathbf{I} + \tau \quad , \quad (5)$$

where p is the pressure. The extra stress tensor is here assumed to satisfy the generalized Newtonian model :

$$\tau = 2 \eta \mathbf{D}^d \quad , \quad (6)$$

where the shear viscosity η is expressed as

$$\eta = \eta (T, p, \alpha_v^c, \dot{\gamma}) \quad , \quad (7)$$

$$\text{with } \dot{\gamma} = \sqrt{2 \mathbf{D}^d : \mathbf{D}^d} \quad , \quad (8)$$

$$\mathbf{D}^d = \mathbf{D} - \frac{1}{3} \text{tr}(\mathbf{D}) \mathbf{I} , \quad (9)$$

$$\mathbf{D} = \frac{1}{2} (\vec{\nabla} \vec{v} + (\vec{\nabla} \vec{v})^t) . \quad (10)$$

In these equations, T , α_v^c and $\dot{\gamma}$ represent the temperature, the relative crystallinity degree and the shear rate, respectively, while $\mathbf{I}$ is the unit tensor and $\mathbf{D}^d$ is the deviatoric part of the rate of deformation tensor. Two models for the steady state shear viscosity are widely used in moulding simulations, namely the power law model :

$$\eta = \eta(T, p, \alpha_v^c, \dot{\gamma}) = \eta_0 \dot{\gamma}^{n-1} , \quad (11)$$

and the Cross model⁶:

$$\eta = \eta(T, p, \alpha_v^c, \dot{\gamma}) = \frac{\eta_0}{1 + \left(\frac{\eta_0 \dot{\gamma}}{\tau_0} \right)^{1-n}} , \quad (12)$$

where $\eta_0 = \eta_0(T, p, \alpha_v^c)$ is the zero shear rate viscosity, while τ_0 and n are material constants. The Cross model fits well the viscosity curves for polymers with a broad molecular weight distribution⁷. These viscosity laws and their impact on the injection moulding model will be investigated in the Chapter V.

The p - v - T -relation

The double-domain Tait equation⁴ is widely used for amorphous polymers. However, this equation does not take into account the density reduction due to crystallization. Moreover, a linear pressure dependence is desirable when computing the pressure field. The following law is therefore used :

$$\rho(T, p, \alpha_v) = \rho_0(T, \alpha_v) + \beta(T, \alpha_v) p , \quad (13)$$

where α_v is the real crystallinity degree. The volume expansion coefficient α , the compressibility coefficient κ and the crystallinity dependence γ are defined as follows :

$$\alpha = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_{p, \alpha_v} , \kappa = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial p} \right)_{T, \alpha_v} \text{ and } \gamma = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial \alpha_v} \right)_{T, p} . \quad (14)$$

The contraction of matter due to crystallization is taken into account thanks to the following relation :

$$\rho(T, p, \alpha_v) = \alpha_v \rho_0^a(T) + (1 - \alpha_v) \rho_0^c(T) + (\alpha_v \beta^a(T) + (1 - \alpha_v) \beta^c(T)) p, \quad (15)$$

where superscripts *a* and *c* indicate the amorphous and crystalline components, respectively.

Thermal properties

The heat flux vector is modelled by the Fourier law :

$$\bar{q} = -\lambda \cdot \nabla T, \quad (16)$$

where λ is the thermal conductivity tensor.

The time derivative of the specific internal energy *e* can be expressed as :

$$\rho \frac{D e}{D t} = \rho c_p \frac{D T}{D t} - \alpha T \frac{D p}{D t} + \frac{p}{\rho} \frac{D \rho}{D t} - \rho \Delta H_m^0 \frac{D \alpha_v}{D t}, \quad (17)$$

where c_p is the thermal capacity at constant hydrostatic pressure and ΔH_m^0 is the latent heat of crystallization. This equation is derived under the assumption that elasticity has a negligible contribution to the mechanical dissipation.

Crystallization kinetics

When dealing with semi-crystalline polymers, crystallization kinetics must be considered.

$$\frac{D \hat{\alpha}_v}{D t} = \hat{\alpha}_v(T, p, \dot{\gamma}, \alpha_v). \quad (18)$$

However, most of the time, α_v is not sufficient to represent the crystalline state of the polymer. For example, in our case, a crystallization model with many parameters has been developed in Chapter III. It must therefore be considered as a vector ($\hat{\alpha}_v$) including as component, the real crystallinity degree α_v in first place and the additional state variable ($\theta_i, \alpha_{vi}^c, N_1, R_1, S_1, V_1$) afterwards. There is one kinetic equation for each state variable and $\hat{\alpha}_v$ is then a set of functions.

2.3. Boundary conditions

A thin cavity is considered, which defines a space domain in space Ω (see Fig. IV.1). The upper and lower surfaces bounding the cavity are denoted by Γ^+ and Γ^- , respectively. These boundaries are impenetrable and the thickness h is assumed to smoothly vary along the mid-plane of the cavity Γ_0 . At time $t=0$, the process starts as the molten polymer flows in the mould cavity through the gate which is denoted by Γ_e . As time progresses, a certain region of the mould cavity $\Omega(t)$ is occupied by the polymer. This region is bounded by the surfaces Γ^+ and Γ^- , the entry section Γ_e , the lateral impenetrable boundaries Γ_w and the melt front $\Gamma_f(t)$. The melt front is the moving boundary between the polymer and the air in the mould cavity. The outer surface of the mould, where the coolant temperature may be prescribed, is denoted by Γ_m .

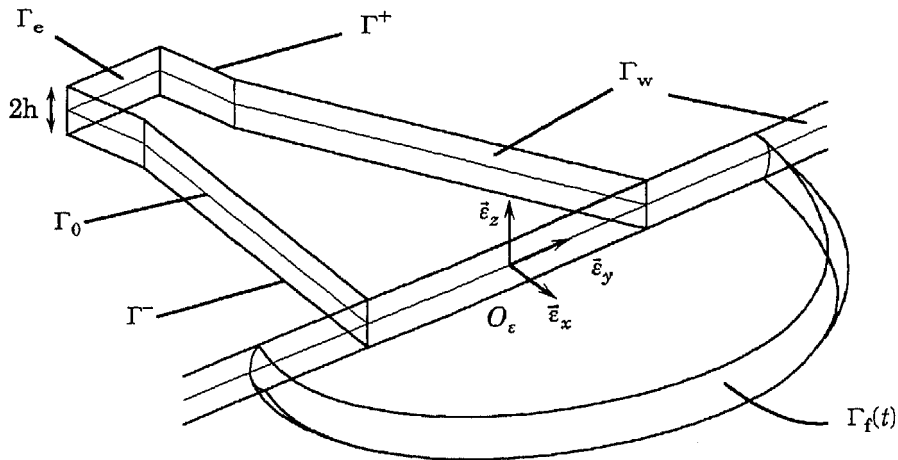


Figure IV.1 : Description of the boundaries of the mould cavity.

The time interval of interest is $\Theta_m = [0, t_e]$ (see Fig. IV.2), where at $t=t_e$ the product is ejected from the mould. This interval is subdivided into three sub-intervals; namely the filling, packing and cooling stages ($\Theta_f, \Theta_p, \Theta_c$). During the time interval $\Theta_f = [0, t_{ef}]$, it is assumed that the volume flux or the pressure is imposed in the inlet section. At time $t_{ef} (< t_e)$, either the mould is completely filled or the

maximum pressure is reached, depending both on the mould and the injection moulding machine. For $t \in \Theta_p = [t_{ef}, t_{ep}]$, the inlet pressure is assumed to be known. At time t_{ep} , the gate is completely solidified. For $t \in \Theta_c = [t_{ep}, t_e]$, no more material is thus allowed to enter the mould and a no-flow inlet condition is imposed.

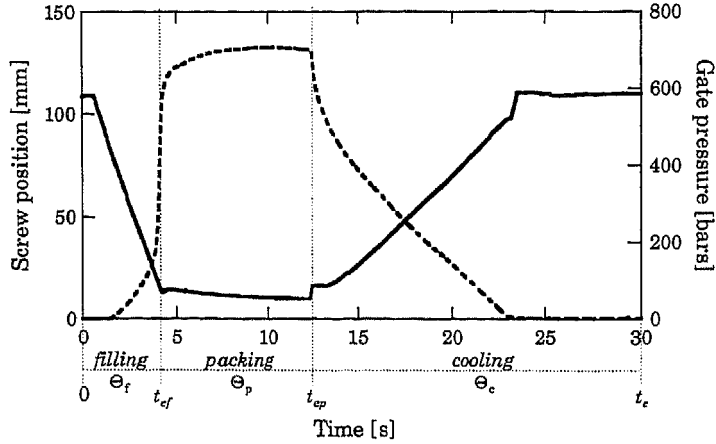


Figure IV.2 : Typical gate pressure (- - -) and screw position (———) as a function of time for a complete injection moulding cycle. Experimental result obtained in collaboration with the Pôle Européen de Plasturgie, Oyonnax, France. The filling, packing and cooling stages are easily identified.

3. The injection moulding model

In this section, major simplifications, that are consistent with the injection moulding process, are introduced in order to simplify the above equations. This will provide us the final form of the process mathematical model.

The mould is assumed to be rigid, in such a way that the pressure field does not affect the dimensions of the cavity. For the sake of simplicity, we will also suppose that the thermal conductivity and the specific heat of the polymer are constant.

3.1. Thin film approximation

The most important simplifying assumption is of a geometrical type. Indeed, in practical applications, the thickness of an injection moulded part is small (0.5-4 mm) as compared to the other dimensions. This thickness is bounded by a maximum value to avoid excessive cooling times and by a minimum value to avoid premature stoppage of the flow and to ensure that the part has sufficient strength. The mould cavity thus consists of narrow, weakly curved channels. This means that the mould is thin, in the sense that one characteristic dimension (the thickness h) is much smaller than the others :

$$\varepsilon = \frac{h}{L} \ll 1 \quad . \quad (19)$$

The second assumption consists in considering the cavity geometry as being formed by a set of (planar or not) surfaces along which the thickness can be smoothly variable. On the basis of geometrical considerations, a complex geometry can be transformed into a set of such surfaces separated by thickness discontinuities or bifurcations. These cases require a special analysis^{8,9} which will not be considered in this thesis. We will limit our description to moulds with a plane mid-surface.

In every point of the mid-plane, a local Cartesian vector base is constructed $O_i : \{\bar{\varepsilon}_x, \bar{\varepsilon}_y, \bar{\varepsilon}_z\}$ (see Fig. IV.1). Note that $\bar{\varepsilon}_z$ is normal to the mid-plane. Any given vector $\bar{a}$ can be split in a vector $\bar{a}_\alpha$, parallel to the mid-plane, and a component in the gapwise direction $\bar{\varepsilon}_z$:

$$\bar{a} = a_i^e \bar{\varepsilon}_i = \bar{a}_\alpha + a_z^e \bar{\varepsilon}_z \quad . \quad (20)$$

Because of the high viscosity of polymer melts, the Reynolds number (i.e. the ratio between inertia and viscosity forces) is small, together with the ratio between the Reynolds and Froude numbers (which is the ratio between body and viscosity forces). Therefore, the inertia and body forces that appear in the momentum equation (2) may be neglected with respect to the viscous forces.

Using the thin film model, the following approximations can be introduced :

-- the pressure is constant in the gapwise direction;

- the in-plane component of the gradient of any quantity is small as compared to that in the $\bar{\varepsilon}_z$ direction. This is in particular true for the gradient of velocity components;
- the velocity components in the $\bar{\varepsilon}_z$ direction are small as compared to those tangent to the mid-plane;
- the in-plane thermal conduction component is negligible with respect to conduction in the $\bar{\varepsilon}_z$ direction. Conduction in the gapwise direction will therefore be taken into account while thermal conduction through lateral boundaries will be neglected;
- no slip is assumed along the walls which are parallel to the mid-surface, while free slip is assumed along the lateral boundaries.

It is also often assumed that the flow is symmetric with respect to the mid-surface. Such hypotheses are classical in the analysis of injection moulding, although their validity must be questioned for certain kinds of flows. For example, one may expect a non-symmetric flow in some parts of the geometry¹⁰; it is the case, especially, beyond bifurcations^{8,11}. Moreover, it is quite difficult to insure the perfect symmetrical cooling of the mould when complex products are fabricated. The classical symmetric Hele Shaw model can however easily be extended to non-symmetric situations.

In the filling of thin cavities, two flow regimes can be distinguished, namely the main Hele Shaw flow and a front flow (see Fig. IV.3). In the main flow domain, a simple 2D stratified flow situation exists, while the fountain flow characterises the motion in the advancing front region. In order to understand the details of this latter flow, we can consider a cross-section of a cavity near the moving front and observe the flow in an Eulerian reference frame moving with the front. Fig. IV.4 shows the finite element mesh and the streamlines obtained by numerical simulation¹². The fountain shape of the streamlines justifies the name of the flow¹³. The melt at the centre of the cavity, which moves with a high velocity, spills out towards the mould walls to form the skin of the moulded part at that location. This is the only way to fill the region located near the walls of the mould, along which there is no slip.

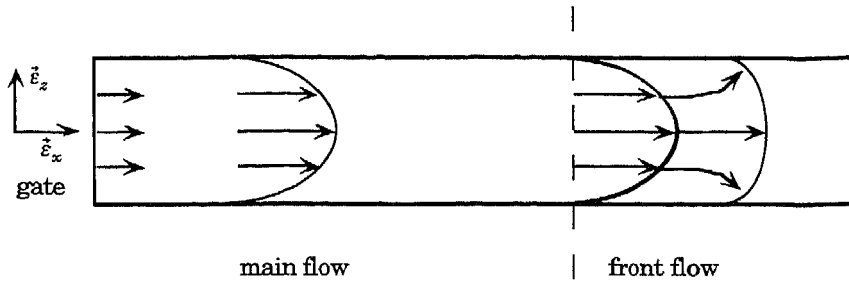


Figure IV.3 : Sketch of the fountain flow.

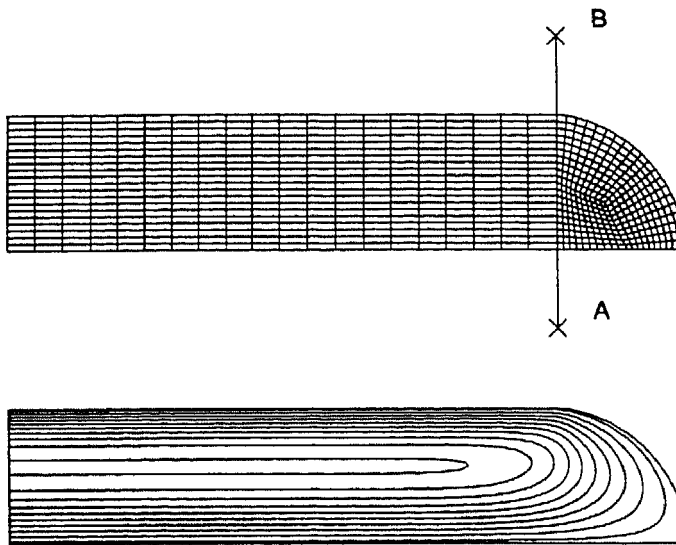


Figure IV.4 : Finite element mesh and streamlines in the fountain flow region (from Crochet et al.¹⁴).

Fountain flow is a major characteristic of mould filling because it affects the particle distribution in moulded products, especially for material elements close to the mould walls. This effect is of major importance in determining the quality and morphology of the surface of moulded articles as well as the nature of weld-lines.

3.2. Simplified set of equations

As a consequence of the simplifications resulting from the thin film approximation, the deviatoric part of the rate of deformation tensor is reduced to

$$\mathbf{D}^d = \frac{1}{2} \frac{\partial}{\partial z} (\tilde{v}_\alpha \tilde{e}_z + \tilde{e}_z \tilde{v}_\alpha) \quad , \quad (21)$$

and the shear rate is given by

$$\dot{\gamma} = \left| \frac{\partial \tilde{v}_\alpha}{\partial z} \right| \quad . \quad (22)$$

Substitution of these simplifications in the constitutive equations and subsequent substitution into the balance equations, results in the following system of equations :

$$\frac{\partial \rho}{\partial t} + \bar{\nabla}_\alpha (\rho \tilde{v}_\alpha) + \frac{\partial \rho w}{\partial z} = 0 \quad , \quad (23)$$

$$\bar{\nabla}_\alpha p = \frac{\partial}{\partial z} \left(\eta \frac{\partial \tilde{v}_\alpha}{\partial z} \right) \quad , \quad \frac{\partial p}{\partial z} = 0 \quad , \quad (24)$$

$$\rho c_p \frac{D T}{D t} = \frac{\partial}{\partial z} \left(k \frac{\partial T}{\partial z} \right) + \eta \dot{\gamma}^2 + \alpha T \frac{D p}{D t} + \rho r \quad . \quad (25)$$

The set of equations (23) to (25) comprises five equations, in which five unknowns – two scalars p , T and three velocity components $\tilde{v}_\alpha$, w – appear. This system of equations is instationary, non-linear and coupled because the viscosity and density are temperature and pressure dependent. In the case of incompressible, isothermal flow, the well-known Hele-Shaw flow model is obtained¹⁵. For details concerning these questions, the reader is referred to Vanderschuren¹⁶, Boshouwers¹⁷ and Kennedy¹⁸.

The pressure equation is derived by eliminating the velocity components from Eqs. (23) and (24). This is achieved by integrating these relations over the thickness of the cavity, yielding an equation where pressure is the only unknown variable. This procedure is a result of Eq. (24b).

Integrating the balance of momentum equation with respect to the thickness coordinate z yields

$$\frac{\partial \tilde{v}_\alpha}{\partial z} = \frac{1}{\eta} (z \bar{\nabla}_\alpha p + \tilde{c}_\alpha) \quad , \quad (26)$$

where $\bar{c}_\alpha$ is an integration constant. As the velocity is assumed to be zero on the walls, this equation can be integrated from $-h$ to z , yielding $\bar{v}_\alpha$ as a function of z :

$$\bar{v}_\alpha(z) = \int_{-h}^z \frac{\partial \bar{v}_\alpha(\xi)}{\partial \xi} d\xi = \bar{\nabla}_\alpha p \int_{-h}^z \frac{\xi}{\eta} d\xi + \bar{c}_\alpha \int_{-h}^z \frac{1}{\eta} d\xi \quad (27)$$

Both $\bar{\nabla}_\alpha p$ and $\bar{c}_\alpha$ are independent of z . The integration constant $\bar{c}_\alpha$ is found from the boundary condition $\bar{v}_\alpha(z=h) = 0$:

$$\bar{c}_\alpha = -\frac{J_1}{J_0} \bar{\nabla}_\alpha p \quad , \text{ where } J_i = \int_{-h}^h \frac{\xi^i}{\eta} d\xi \quad (28)$$

Substitution of Eq. (28) in Eq. (27) gives

$$\bar{v}_\alpha(z) = \bar{\nabla}_\alpha p \int_{-h}^z \frac{1}{\eta} \left(\xi - \frac{J_1}{J_0} \right) d\xi = \bar{\nabla}_\alpha p \int_{-h}^z \omega(\xi) d\xi \quad , \quad (29)$$

where $\omega(\xi)$ is called the *profile function*. Note that, if symmetry with respect to the mid-plane is present, $J_1 = 0$. The w velocity component can be solved from Eq. (29) and the continuity equation (Eq. 23) :

$$\frac{\partial w}{\partial z} = -\bar{\nabla}_\alpha \bar{v}_\alpha - \frac{1}{\rho} \frac{D\rho}{Dt} \quad , \quad (30)$$

together with the boundary condition $w=0$ on the walls.

Partial integration of Eq. (29) over the total channel thickness yields

$$\int_{-h}^h \bar{v}_\alpha d\xi = 2h \bar{\bar{v}}_\alpha = -S_v \bar{\nabla}_\alpha p \quad , \quad S_v = J_2 - \frac{J_1^2}{J_0} \quad , \quad (31)$$

where $\bar{\bar{v}}_\alpha$ is the average velocity and S_v is called the *fluidity*. One can observe that the pressure field p now acts as a potential for the average velocity field; $\bar{\bar{v}}_\alpha$ depends only of x_α , p and h . Similarly, the following relation can be written :

$$\int_{-h}^h \rho \bar{v}_\alpha d\xi = 2h \bar{\bar{\rho v}}_\alpha = -S_p \bar{\nabla}_\alpha p \quad , \quad (32)$$

where the fluidity S_p is defined by

$$S_p = \int_{-h}^h \left(\rho \int_{-h}^z \frac{1}{\eta} \left(\xi - \frac{J_1}{J_0} \right) d\xi \right) dz \quad . \quad (33)$$

Integration of the continuity equation (Eq. 23) over the channel thickness gives

$$\int_{-h}^h \bar{\nabla}_\alpha (\rho \bar{v}_\alpha) d\zeta + \int_{-h}^h \frac{\partial \rho w}{\partial \zeta} d\zeta = - \int_{-h}^h \frac{\partial \rho}{\partial t} d\zeta . \quad (34)$$

The second term of Eq. (34) is zero due to the non-slip boundary condition on the mould walls. Thanks to the no-slip condition at the main walls, substitution of Eq. (32) in Eq. (34) gives :

$$\bar{\nabla}_\alpha \cdot (S_\rho \bar{\nabla}_\alpha p) = \int_{-h}^h \frac{\partial \rho}{\partial t} d\zeta . \quad (35)$$

Because the density ρ depends on the pressure p and the temperature T and crystallinity degree α_v , thus

$$\frac{\partial \rho}{\partial t} = \left(\frac{\partial \rho}{\partial T} \right)_{p, \alpha_v} \frac{\partial T}{\partial t} + \left(\frac{\partial \rho}{\partial p} \right)_{T, \alpha_v} \frac{\partial p}{\partial t} + \left(\frac{\partial \rho}{\partial \alpha_v} \right)_{p, T} \frac{\partial \alpha_v}{\partial t} , \quad (36)$$

Substitution of Eq. (36) and the compressibility coefficients defined in Eq. (14) into Eq. (35) results finally in

$$\bar{\nabla}_\alpha \cdot (S_\rho \bar{\nabla}_\alpha p) = \int_{-h}^h \rho \kappa \frac{\partial p}{\partial t} d\zeta - \int_{-h}^h \rho \alpha \frac{\partial T}{\partial t} d\zeta + \int_{-h}^h \rho \gamma \frac{\partial \alpha_v}{\partial t} d\zeta , \quad (37)$$

where $p \geq 0$. It should be mentioned that S_ρ implicitly depends on p and $\|\bar{\nabla}_\alpha p\|$ through pressure and shear rate dependence of the viscosity.

Finally, a complete three-dimensional analysis would require to solve the energy equation (Eq. 25) :

$$\rho c_p \frac{D T}{D t} = \frac{\partial}{\partial z} \left(k \frac{\partial T}{\partial z} \right) + \eta \dot{\gamma}^2 + \alpha T \frac{D p}{D t} + \rho r . \quad (25)$$

In the material derivative of temperature, the convective terms play a major role in injection moulding because of the large value of the Péclet number defined as follows :

$$Pe = \frac{\rho c_p V L}{k} , \quad (38)$$

where V and L are a characteristic velocity and dimension of the flow in the mid-plane direction, respectively. In the right-hand side of Eq. (25), the heat diffusion and the viscous dissipation terms are important in many injection moulding applications. In the last term, r stands for the heat released per unit mass and time;

it vanishes in the absence of chemical reactions such as curing, or phase transformations such as crystallization.

It should be emphasized that temperature calculation represents a truly three-dimensional problem. In view of the important cooling of the melt through the main walls and the localized heat sources due to viscous dissipation, one cannot reduce the temperature field to its average across the thickness without major losses of accuracy.

3.3. Fountain flow modelling

Since the numerical simulation of injection moulding is based on the Hele Shaw approximation, it is not possible to represent the curvature of the flow front in the gapwise direction. The frontal zone, where the fountain flow occurs, is assumed to be extremely thin with respect to the characteristic dimensions of the part. It is therefore represented in the thin film approximation by a straight rectilinear segment perpendicular to the mid-plane, as shown in Fig. IV.5.

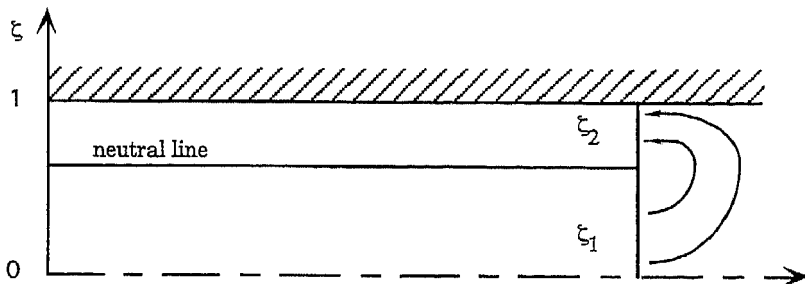


Figure IV.5 : Simplified geometry of the fountain flow region.

Returning to Fig. IV.4, let us draw a vertical line AB just behind the almost circular free surface of the flow front; Fig. IV.6 shows the horizontal velocity profile along AB. One finds that there is a neutral line at which fluid particles are moving at the same velocity as the flow front. Below the neutral line, the frontal region is fed by the fluid particles moving faster than the flow front in the central part of the

mould. Above the neutral line, fluid particles are slower than the flow front. The region, located above the neutral line is thus fed by the central region.

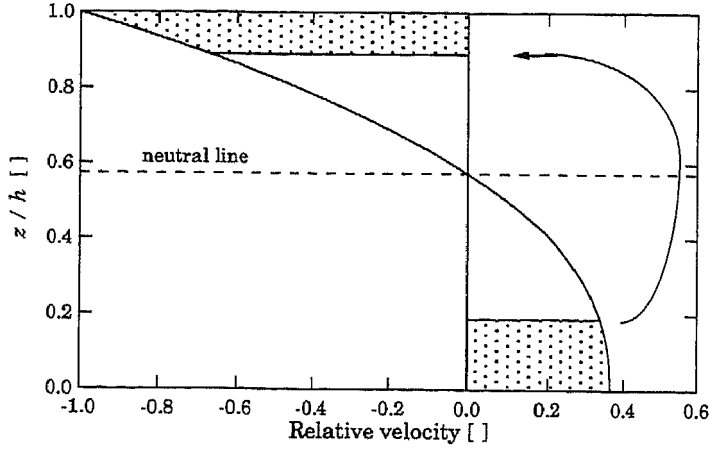


Figure IV.6 : Velocity profile along the vertical line AB of Fig. IV.4.

Dupret and Vanderschuren²⁵ have solved the problem by establishing an equivalence between the nodes located below and above the neutral line. Manas-Zloczower *et al.*¹⁹ have independently used the same approach for calculating residence times in the RIM process. For values of ζ below the neutral line, the values of T on the flow front are not constrained by any condition. For ζ above the neutral line, the values of T on the flow front are subject to the boundary condition :

$$T(\zeta_2) = T(\zeta_1) \quad . \quad (39)$$

The pair $[\zeta_1, \zeta_2]$ is such that a material point which enters the frontal zone at an ordinate $\zeta_1 = \frac{z_1}{h}$ leaves this zone at an ordinate ζ_2 which is calculated thanks to the relation

$$\int_0^{\zeta_1} (v_\alpha(z) - \bar{v}_\alpha) dz = \int_{\zeta_2}^h (\bar{v}_\alpha - v_\alpha(z)) dz \quad . \quad (40)$$

Eq. (39) neglects the influence of heat diffusion and viscous heating in the frontal zone. Such an assumption, which is based on a singular perturbation analysis of the system, is the only way to introduce a fountain flow model consistent

with the Hele-Shaw approximation²⁰. The correct handling of fountain flow in the Hele Shaw model has major consequences on the evaluation of the time dependent temperature field. Any other approach leads to a lack of energy balance during the filling process.

3.4. Calculation of the crystallinity degree

Crystallization is a phase transformation which highly depends on temperature, pressure and shear, resulting in a full 3D field in the injection moulding process. Two methods for calculating the crystallinity field have been analysed.

The first method is based on a fully coupled calculation, which simultaneously performs the computation of temperature, pressure, velocity and crystallinity fields during the process. The full system of equations is completed with a differential form of the crystallization model. This first method is expensive, but accurate, since it takes into account the influence of crystallization both on the flow (through its impact on viscosity and density) and on the heat transfer (through the release of crystallization heat). However, only differential models of crystallization can be easily treated by this technique.

A second and decoupled method has been investigated, which assumes that crystallization does not play a significant role during the process. Hence, its influence on the flow and the temperature field can be neglected. In a first step, temperature and pressure fields are computed without taking the influence of crystallization into account, and the successive results are stored. The crystallinity degree is estimated in a subsequent step by integrating the crystallization kinetic equations from the thermomechanical (i.e. temperature, pressure, shear stress, ...) histories of selected injected particles. These thermomechanical histories are obtained by means of a tracking algorithm, which reconstructs the trajectory of any given material point in the part by means of an explicit Euler integration scheme²¹. It is thus possible to recover from a previous computation the values of the different fields at any time of the process and to reconstruct their histories for every selected material point. Details concerning the tracking scheme are given in Section 5. This

second method, while being less accurate than the fully coupled calculation, has a lower computational cost and integral models of crystallization can easily be used.

3.5. Boundary conditions

Let us first recall that the injection moulding process is divided into three stages – filling, packing and cooling – during which specific boundary conditions must be imposed.

The pressure problem reduces in the solution of Eq. (37) with the following boundary conditions :

– Along the lateral walls Γ_w , during the whole process Θ_m , a vanishing normal velocity and thus, in view of Eq. (29), a vanishing normal pressure gradient is imposed :

$$\bar{\nabla}_\alpha p \cdot \bar{n} = 0 \quad . \quad (41)$$

Note that, in the calculation of the average velocity field, the fluid is assumed to slip along these walls; the Hele Shaw approximation indeed neglects the presence of a boundary layer (whose thickness is of order h) where the effect of the lateral wall is important.

– For the sake of simplicity, the runner system will not be considered. At the gate Γ_g , either the pressure (which may be time-dependent) or the normal pressure gradient (corresponding to a fixed flow rate) is imposed during the filling stage Θ_f , while, during the packing stage Θ_p , the holding pressure is imposed.

– On the flow front $\Gamma_f(t)$, the pressure p is imposed to atmospheric pressure. The resulting normal velocity :

$$\bar{v}_n = -\frac{S}{h} \frac{\partial p}{\partial n} \quad (42)$$

allows to calculate the motion of the flow front.

The temperature problem reduces to the solution of Eq. (25) with the following boundary conditions :

– At the gates Γ_e , during the filling time Θ_f , it is usually assumed that the fluid has an imposed uniform temperature; one may possibly impose a non-uniform temperature, but this would require an accurate temperature calculation in the feeding channels and the gates²². The relaxation method developed by Dheur¹¹ takes the cooling of the gate into account when velocities are low (as encountered during the packing and cooling stages).

– Along the lateral walls Γ_w , we are not entitled to introduce any boundary condition because the heat diffusion terms in the mid-surface are neglected in Eq. (25).

– On the upper and lower walls Γ^- and Γ^+ , the effect of the mould, which cools the melt but which is also warmed up by it, is taken into account by special conditions as developed by Dheur¹¹ and Mal²³.

Finally, we need to specify boundary conditions at the flow front $\Gamma_f(t)$. In the case of a truly three-dimensional problem, we would simply impose that the normal heat flux vanishes on the moving surface, or that there is no heat transfer between the melt and the surrounding gas. However, the problem is complicated by the Hele Shaw approximation, which neglects the presence of a front boundary layer. A special treatment is therefore needed for handling the fountain flow effect. This problem has been addressed in Section 3.3.

4. Numerical simulation of injection moulding

In the present section, a numerical method will be described for calculating the pressure, velocity, temperature and crystallinity fields during the whole process, together with the moving boundary of the domain during the filling stage. This algorithm is an extension of previous work by Dupret's group^{1,11,16,24}.

4.1. Spatial discretisation and algorithm

Let us first give an overview of the successive steps of the algorithm. Fig. IV.7, shows the mid-surface Γ_0 of a mould of gap width $2h$. At time t_n , a portion

Γ_n of the mid-surface is filled with fluid which is fed through the gate Γ_e . The domain Γ_n is covered by a finite element mesh Γ_n^h delimited by the boundary $\partial\Gamma^h$. Superscript h denotes the finite element representation of the field which is calculated. In order to compute the temperature and velocity profiles, the gapwise direction must also be discretized. A collocation technique has been selected (following the method of Dupret and Vanderschuren²⁵), in which m collocation points are defined in the interval $[-1,1]$ using the normalised thickness coordinate ξ :

$$\xi_j = \frac{z_j}{h} \quad 1 \leq j \leq m \quad . \quad (43)$$

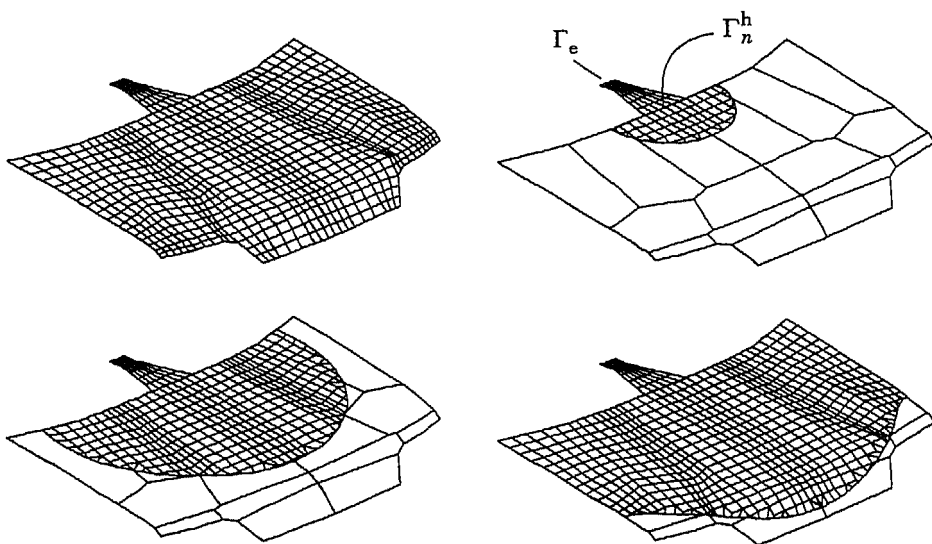


Figure IV.7 : Changing flow domain of a car bonnet part: initial finite element mesh and successive flow fronts, together with the associated meshes.

Starting with the finite element mesh Γ_n^h on which the temperature field T_n^h has been calculated, the time is incremented by an amount Δt . The successive steps of the calculation are as follows :

- i. calculation of the pressure field P_n^h on Γ_n^h ;
- ii. calculation of the velocity field V_n^h on Γ_n^h ;

- iii. calculation of a provisional temperature field $\hat{T}_{n+1}^h$ on Γ_n^h ;
- iv. calculation of the new flow domain Γ_{n+1} and the new mesh Γ_{n+1}^h ;
- v. extension of $\hat{T}_{n+1}^h$ to T_{n+1}^h on Γ_{n+1}^h .

which is reduced to step i. to iii. during the cooling and the packing stages.

4.2. Calculation of the pressure field P_n^h

For calculating the pressure field P^h at a given time t over the finite element mesh Γ^h , we need to solve Eq. (37) with appropriate boundary conditions. The pressure is approximated by a finite element representation

$$P^h = \sum_i P_i \psi_i(x, y) \quad , \quad (44)$$

where the P_i 's are the nodal values and the ψ_i 's are the shape functions. In this study, biquadratic shape functions on nine node quadrilateral elements or second-order polynomials on six-node triangles are used. The discretized form of Eq. (37) is obtained by means of the Galerkin method, i.e. for every shape function ψ_i one writes

$$\begin{aligned} \int_{\Gamma^h} \left(- \int_{-h}^h \rho \kappa \frac{\partial P^h}{\partial t} d\zeta + \int_{-h}^h \rho \alpha \frac{\partial T^h}{\partial t} d\zeta - \int_{-h}^h \rho \gamma \frac{\partial \alpha_v^h}{\partial t} d\zeta \right) \psi_i \\ + S_\rho \left(\frac{\partial P^h}{\partial x} \frac{\partial \psi_i}{\partial x} + \frac{\partial P^h}{\partial y} \frac{\partial \psi_i}{\partial y} \right) d\Omega = \int_{\partial\Gamma^h} S_\rho \frac{\partial P^h}{\partial n} \psi_i d\sigma \quad . \quad (45) \end{aligned}$$

Replacing P^h by its finite element representation (Eq. (44)), one obtains

$$\begin{aligned} \sum_j \left(- \left[\int_{\Gamma^h} \int_{-h}^h \rho \kappa d\zeta \psi_i \psi_j d\Omega \right] \dot{P}_j + \left[\int_{\Gamma^h} S_\rho \left(\frac{\partial \psi_i}{\partial x} \frac{\partial \psi_j}{\partial x} + \frac{\partial \psi_i}{\partial y} \frac{\partial \psi_j}{\partial y} \right) d\Omega \right] P_j \right) \\ = - \left[\int_{\Gamma^h} \int_{-h}^h \rho \left(\alpha \frac{\partial T^h}{\partial t} - \gamma \frac{\partial \alpha_v^h}{\partial t} \right) d\zeta \psi_i d\Omega \right] - \left[\int_{\partial\Gamma^h} 2 h \bar{\rho} \bar{v}_n \psi_i d\sigma \right] \quad , \quad (46) \end{aligned}$$

where Eq. (32) has been introduced. We note that, on the boundary $\partial\Gamma^h$, one of the following conditions prevails : P_j is known (at the flow front), $\bar{\rho} \bar{v}_n$ vanishes (on lateral walls), or $\bar{\rho} \bar{v}_n$ is known (in an entry section). The thickness h may be slightly variable upon the cavity; under such conditions, we assume that, within an element, there exists a representation

$$h = \sum_i h_i \psi_i(x, y) \quad . \quad (47)$$

Eqs. (46) finally reduce to a non-linear system of the form

$$\sum_j (A_{ij} \dot{P}_j + B_{ij}(P^h) P_j) = C_i + D_i \quad , \quad (48)$$

where

$$A_{ij} = - \int_{\Gamma^h} \int_{-h}^h \rho \kappa d\zeta \psi_i \psi_j d\Omega \quad , \quad (49)$$

$$B_{ij}(P^h) = \int_{\Gamma^h} S_\rho \left(\frac{\partial \psi_i}{\partial x} \frac{\partial \psi_j}{\partial x} + \frac{\partial \psi_i}{\partial y} \frac{\partial \psi_j}{\partial y} \right) d\Omega \quad , \quad (50)$$

$$C_i = - \int_{\Gamma^h} \int_{-h}^h \rho \alpha \frac{\partial T^h}{\partial t} - \gamma \frac{\partial \alpha_v^h}{\partial t} d\zeta \psi_i d\Omega \quad , \quad (51)$$

$$D_i = - \int_{\Gamma_e} 2h \bar{\rho} \bar{v}_n \psi_i ds \quad , \quad (52)$$

where the essential front boundary conditions are taken into account by imposing $P_i = 0$ on $\Gamma_f(t)$, together with dropping the front test functions, in such a way that $\psi_i = 0$ on $\Gamma_f(t)$. It must be mentioned that matrices A_{ij} and C_i are also pressure dependent when dealing with density laws which are not purely linear in pressure.

A new challenge is now posed as one must calculate the integral S_ρ in Eq. (33), which depends upon the pressure field through the shear rate dependence of the viscosity. Usually, power-law viscosities are used, which allows to factor out the pressure gradient contribution in the calculation of the fluidity¹⁶. As the fluidity is the result of an integration in the gapwise direction, factoring out the effect of pressure in the calculation of the fluidity is the only way to avoid that costly integrations be embedded in pressure iterations. A single integration in the gapwise direction is therefore required per time step in order to solve for the pressure field when a power-law viscosity is used. The power-law model is unfortunately far from satisfactory in many circumstances of practical interest. A new and cheap method for introducing complex viscosity laws such as the Cross or Carreau laws was thus developed. In this method, which will be detailed in Chapter 5, the Cross law is

approximated by an accurate expansion that presents most of the numerical advantages of the power-law viscosity.

4.3. Calculation of the velocity field on Γ_n^h .

Velocities are present in the convective terms of the temperature equation, which are evaluated at each integration point of the elements covering the mid-plane. As, with our decoupled scheme, the pressure field is known during velocity calculations, pressure gradients are easily evaluated at the integration points and in-plane velocities (u and v) are then evaluated thanks to Eq. (29) as long as the profile function $\omega(z)$ is known.

The displacement of the flow front, the particle tracking algorithm and also the computation of the w velocity component however require the knowledge of in-plane velocity components (u and v) at each node of the finite element mesh. This is achieved by using the Galerkin method on each element, which provides a discontinuous velocity field. As velocity profiles are easily calculated from the average velocities thanks to Eqs. (29) and (31), this method must be applied to the average velocity field only. In-plane velocity components are approximated as follows :

$$\bar{v}_\alpha^h = \sum_i \bar{v}_{\alpha,i} \varphi_i(x, y) \quad , \quad (53)$$

where the summation refers to the nodes of Γ_n^h , the $\bar{v}_{\alpha,i}$'s are the nodal velocities and the φ_i 's are shape functions in the mid-surface. We have selected bilinear shape functions over quadrilaterals and first order polynomials over triangles. The discretized form of the velocity equation (Eq. 31) is obtained by means of the Galerkin method, which is separately applied on each element of the mesh :

$$\int_{\Gamma^h} \bar{v}_\alpha^h \varphi_j \, d\Omega = \int_{\Gamma^h} \frac{\bar{\nabla}_\alpha p}{2h} \frac{S_v}{S_v} \varphi_j \, d\Omega \quad , \quad (54)$$

This method allows us to easily introduce appropriate boundary conditions along the lateral impenetrable walls of the cavity. Indeed, as velocities are derived from the pressure field, and as natural pressure boundary condition are imposed on these walls, the computation of the velocities normally generates a small normal velocity

component on these walls, which must however be imposed to be zero. Using the discontinuous method works better than using the Galerkin method on the whole mesh (which results in a continuous velocity) field due to the fact that, in that case, oscillations are generated when a zero normal velocity component is imposed.

Once the average velocity field is known, velocity profiles are easily calculated with Eq. (29). The gapwise derivative of the profile function $\omega(z)$ is approximated by means of cubic splines passing by the collocation points, with natural extremity conditions. Velocity profiles are then easily obtained by simple integration of the profile functions.

The w velocity, however, cannot be obtained from its average value (which is equal to zero). Nevertheless, it is possible to compute this component thanks to the continuity equation (Eq. 23). To the end, we first decompose w (as shown in Fig. IV.8) into a first component ($\bar{w}$) related to thickness variation (it is exactly the w velocity in the case of an isothermal Newtonian flow) and a second component (w^*) due to possible changes of layer experienced by the material points :

$$\bar{w} = \frac{z}{h} \left(u \frac{\partial h}{\partial x} + v \frac{\partial h}{\partial y} \right), \quad (55)$$

$$w^* = h \frac{D\xi}{Dt} = \frac{Dz}{Dt} - \frac{z}{h} \left(u \frac{\partial h}{\partial x} + v \frac{\partial h}{\partial y} \right) = w - \bar{w} \quad (56)$$

Material points which are moving at constant normalised thickness coordinate (which is defined by $\xi = z/h$) implicitly move with the velocity $\bar{w}$. Derivation of Eq. (56) yields

$$\frac{\partial w^*}{\partial z} = \frac{\partial w}{\partial z} - \frac{\partial \bar{w}}{\partial z} = \frac{\partial w}{\partial z} - \frac{1}{h} \left(u \frac{\partial h}{\partial x} + v \frac{\partial h}{\partial y} \right) - \frac{z}{h} \left(\frac{\partial u}{\partial z} \frac{\partial h}{\partial x} + \frac{\partial v}{\partial z} \frac{\partial h}{\partial y} \right), \quad (57)$$

and, replacing $\frac{\partial w}{\partial z}$ by its value provided by the continuity equation, one obtains :

$$\frac{\partial w^*}{\partial z} = - \left(\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} \right) - \frac{1}{\rho} \frac{D\rho}{Dt} - \frac{1}{h} \left(u \frac{\partial h}{\partial x} + v \frac{\partial h}{\partial y} \right) - \frac{z}{h} \left(\frac{\partial u}{\partial z} \frac{\partial h}{\partial x} + \frac{\partial v}{\partial z} \frac{\partial h}{\partial y} \right), \quad (58)$$

As u and v velocity components are calculated layer by layer, $u(\xi)$, $v(\xi)$ and their derivatives $\frac{\partial u(\xi)}{\partial \xi}$ and $\frac{\partial v(\xi)}{\partial \xi}$ or $\frac{\partial u(\xi)}{\partial z}$ and $\frac{\partial v(\xi)}{\partial z}$, are known. It is easy to show that :

$$\begin{aligned}\left. \frac{\partial u(z)}{\partial x} \right|_z &= \left. \frac{\partial u(\xi)}{\partial x} \right|_\xi - \xi \frac{\partial h}{\partial x} \left. \frac{\partial u(\xi)}{\partial z} \right|_x \\ \left. \frac{\partial v(z)}{\partial y} \right|_z &= \left. \frac{\partial v(\xi)}{\partial y} \right|_\xi - \xi \frac{\partial h}{\partial y} \left. \frac{\partial v(\xi)}{\partial z} \right|_y\end{aligned}\quad (59)$$

Eq. (58) can therefore be written in the form :

$$\frac{\partial w^*}{\partial z} = - \left(\frac{\partial u(\xi)}{\partial x} + \frac{\partial v(\xi)}{\partial y} \right) - \frac{1}{\rho} \frac{D\rho}{Dt} - \frac{1}{h} \left(u(\xi) \frac{\partial h}{\partial x} + v(\xi) \frac{\partial h}{\partial y} \right) \quad (60)$$

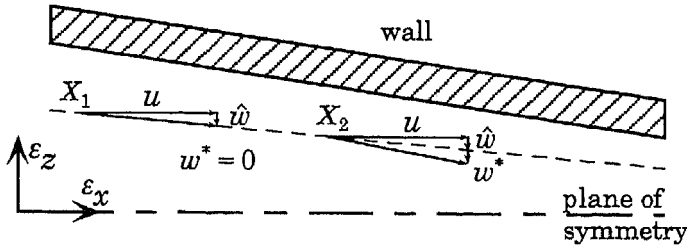


Figure IV.8 : Decomposition of the w velocity component into $\hat{w}$ and w^* in case of isothermal simulation (X_1) and non-isothermal simulation (X_2).

Finally, $\frac{\partial w^*}{\partial z}$ is made discrete in the same manner as in-plane velocities, and can thus be obtained at every node thanks to the Galerkin technique. Influence of the w velocity on typical injection moulding results and demonstration of its non-negligible contribution are given in Chapter 6.

4.4. Calculation of a provisional temperature field $\hat{T}_{n+1}^h$ on Γ_n^h .

It was already mentioned that the temperature field is three-dimensional, while partial time derivatives appear in the left-hand side of Eq. (25). Moreover, the numerical method must take into account the fact that heat diffusion takes place in the transverse direction, while convection is mainly effective along the mid-surface. The numerical method developed by Dupret and Vanderschuren²⁵ combines the Galerkin method in the mid-surface together with Chebyshev collocation in the transverse direction. The latter technique is justified by the high temperature gradients encountered near the walls of the cavity in injection moulding applications. This technique was subsequently improved by Mal *et al.*²⁶, who developed a

"decomposition technique" for the temperature field based on the assumption that, during the first instants following the fountain flow, heat transfer between the cold wall and the hot melt is governed by a thermal shock. The temperature profile is, therefore, very steep and, in practice, unwanted numerical oscillations are generated when classical methods are used. In order to get rid of these oscillations, the temperature profile is split in two components, the first one being given by an analytical shock solution which captures the steep profile, while the other component is unknown, but smooth, and can be calculated by solving the energy equation. The temperature is approximated as follows :

$$T^h = \sum_i T_i(\xi) \varphi_i(x_\alpha) \quad , \quad (61)$$

where the summation refers to the nodes of Γ_n^h , the φ_i 's are shape functions in the mid-surface, and $T_i(\xi)$ is a temperature profile throughout the thickness at node i and time t . Similar shape functions are selected as for velocity calculations. Along the z -direction, a cubic spline approximation is used, which is much more efficient than the previously used Lagrange polynomials, since temperature oscillations in the gapwise direction are more efficiently damped out^{11,16}.

From spatial discretization of the energy equation, one obtains the following semi-discrete equations at each node and collocation point :

$$\left\{ \begin{aligned} \left(\frac{\partial T_j}{\partial t} \right)_{\xi=\xi_\alpha} &= \frac{k}{\rho c_p h_j^2} \left(\frac{\partial^2 T_j}{\partial \xi^2} \right) + f_{j\alpha} \\ \sum_{j=1}^N \left[\int_{\Gamma^h} \tilde{\varphi}_i \varphi_j \right] f_{j\alpha} &= \int_{\Gamma^h} \left(-\dot{v} \cdot \vec{\nabla} T + \frac{1}{\rho c_p} \left(\eta \dot{\gamma}^2 + \alpha T \frac{Dp}{Dt} + \rho r \right) \right)_{\xi=\xi_\alpha} \tilde{\varphi}_i d\Omega . \end{aligned} \right. \quad (62)$$

The full system of equations therefore reduces to

$$[\dot{y}_j] = K(t) [y_j] + g_f([y_j], P, t) \quad , \quad (63)$$

where $[y_j] = [(T_j)_{\xi=\xi_1}, \dots, (T_j)_{\xi=\xi_m}]^T$ are the temperature unknowns.

Several wall boundary conditions have been analysed previously (including, in particular, a constant thermal thickness model¹⁶ and a variable thermal thickness model¹¹). Finally, as the boundary condition is mainly governed by a thermal shock

between the molten polymer and the cold wall, a simplified model of the analytical thermal shock between two bodies is used²⁶. The temperature profile is thus split into two components, where T_i^a is the analytical component, taking into account the thermal shocks on the pair of walls, while T_i^* is a calculated component, which is obtained by solving the energy equation and is represented by means of cubic splines :

$$T_i(z, t) = T_i^*(z, t) + T_i^a(z, t) , \quad (64)$$

$$\text{and} \quad T_i^a(z, t) = (T_{im} - T_{iw}^+) \operatorname{erfc}\left(\frac{h_i - z}{\sqrt{4 \frac{k}{\rho c_p} (t - t_{i0})}}\right) + (T_{im} - T_{iw}^-) \operatorname{erfc}\left(\frac{h_i + z}{\sqrt{4 \frac{k}{\rho c_p} (t - t_{i0})}}\right) .$$

where T_{im} , T_{iw}^+ and T_{iw}^- are the polymer melt, upper and lower mould temperatures while t_{i0} is the time at which the polymer enters in contact with the mould.

Time integration is performed by means of a third order mixed explicit-implicit scheme. Briefly, an explicit Runge-Kutta method is used for integrating the advective terms of the right-hand side of Eq. (62), while, for stability reasons, the diffusive terms are implicitly integrated. Details on the time integration scheme may be found in Dupret and Vanderschuren²⁵ and in Mal²³.

4.5. Calculation of the new domain Γ_{n+1}^h

A central problem in the numerical simulation of injection moulding is the time dependency of the flow domain. In practical applications, the complex geometry of the mould generates important changes of size and shape of the filled region. It is in general insufficient to maintain throughout the simulation the topology of the finite element mesh and to simply adapt it to the moving boundary. While Hieber and Shen¹⁵ have used at every time step a full mesh generation over the whole domain, it is also possible to use a remeshing technique based on a preassigned finite element mesh covering the whole domain²⁴. Fig. IV.7 shows a flow domain over which we have generated an initial finite element mesh; a certain number of successive flow fronts are shown together with the associated finite element meshes. It is found that, for all the successive steps, most of the initial mesh is used while remeshing is limited to a region located near the flow front.

Details about remeshing techniques are beyond the scope of the present chapter. It is enough for our present purpose to consider at time t_n a flow domain Γ_n covered by a finite element mesh Γ_n^h (see Fig. IV.9). The calculation of the pressure field P_n^h provides the average velocity field through the cross-section of the mould and, in particular, the velocity of the moving flow front. An explicit scheme provides the location of the front nodes at time t_{n+1} together with an extrapolation mesh Q_{n+1} which defines, in addition to Γ_n , the new flow domain $\hat{\Gamma}_{n+1}$. An automatic remeshing technique covers $\hat{\Gamma}_{n+1}$ by a finite element mesh Γ_{n+1}^h . Due to geometrical considerations (including the constraint to generate well-behaved meshes), the front F_{n+1} does not match exactly the predetermined new front $\hat{F}_{n+1}$ (as obtained by moving the nodes of the previous front F_n). This phenomenon, while having a minor impact on the simulation of filling, has a major impact on the tracking of material particles, as it will be explained in Section 5.

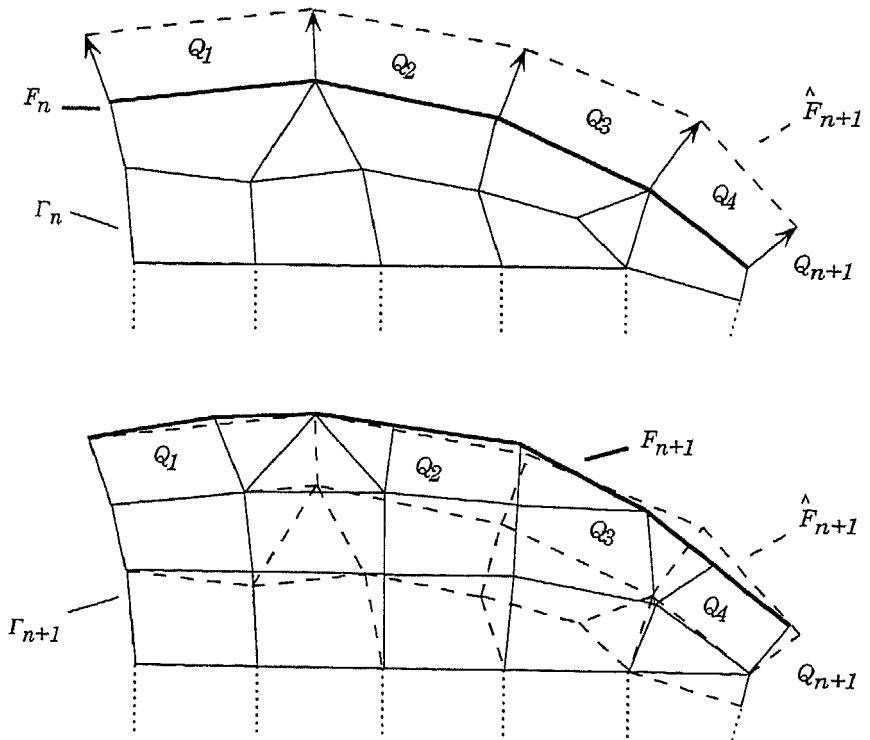


Figure IV.9 : Detail of two successive meshes.

4.6. Calculation of the temperature field T_{n+1}^h over Γ_{n+1}^h .

One of the most delicate problems of the non-isothermal simulation of injection moulding is found at this stage, since the flow domain has been extended from Γ_n^h to Γ_{n+1}^h . Both meshes are different and cover a different domain.

We first wish to extrapolate to $\hat{\Gamma}_{n+1}$ the temperature field $\hat{T}_{n+1}^h$ which has been obtained on Γ_n^h . A straightforward approach consists in minimising the functional :

$$I = \int_{F_n} (\bar{\nabla}_\alpha \hat{T} - \bar{\nabla}_\alpha \tilde{T})^2 ds \quad , \quad (65)$$

for every layer (i.e. every collocation point). In Eq. (65), $\bar{\nabla}_\alpha \hat{T}$ represents the temperature gradient calculated with the provisional temperature field $\hat{T}_{n+1}^h$ on the upstream elements adjacent to the old front F_n (i.e. on Γ_n^h), while $\bar{\nabla}_\alpha \tilde{T}$ represents the temperature gradient calculated with the searched provisional temperature on the downstream elements adjacent to F_n (i.e. on Q_{n+1}).

The results would however be incorrect and in most cases exhibit dramatic deviations with respect to the real flow, because at this stage fountain effect has not been taken into account. The obtained temperature field on $\hat{\Gamma}_{n+1}$ is therefore corrected for fountain flow by means of the model presented in Section 3.3.

Finally, the corrected temperature field $\hat{T}_{n+1}^h$, which is defined on $\Gamma_n^h \cup Q_{n+1}$ is interpolated on Γ_{n+1}^h giving the new temperature field T_{n+1}^h .

Details concerning these methods can be found in Mal²³.

4.7. Calculation of crystallinity (coupled method)

When crystallinity is predicted by means of the coupled method (Section 3.4), the crystallinity fields are integrated in space and time in a similar way as the temperature field. First, provisional crystallinity fields ($\hat{\alpha}_{n+1}^h$) are calculated on the old flow domain Γ_n^h . They are extrapolated in a subsequent step to the new flow domain, taking fountain flow into account. Crystallinity fields are also 3D fields. However, the problem is simplified because there is no diffusion, on the contrary of temperature.

5. The tracking algorithm

For obvious reasons, in the particle tracking technique we have developed, no real particles are present that exert hydrodynamic interaction (as in the flow or the motion of real particles). The particles are abstract distinct material points in the flow that have to be followed in time and space. With this definition, particle tracking received considerable attention in the numerical simulation of non-Newtonian flows with memory integral equations²⁷⁻³¹. Since integral models take into account a part of the deformation history to calculate the Cauchy-Green and Finger strain tensors, it is essential to find the particle position as a function of the residence time. In a similar way, particle tracking has been used in this thesis to evaluate integral crystallization models.

Particle tracking can be carried out by constructing the pathline l of any given particle. The track of a particle during the time interval $[t-s, t]$ can be represented by using a relation of the form

$$\vec{x}_s = \hat{\vec{x}}_s(\vec{x}, t; t-s) \quad . \quad (66)$$

Eq. (66) states that $\vec{x}_s$ is the position at time $t-s$ of a particle which occupies the position $\vec{x}$ at time t . Connecting all successive positions $\vec{x}_s$, with $s \in [0, t]$, the particle pathline is obtained. The trajectory l of a particle which occupies the position $\vec{x}$ at time t can then be expressed as :

$$l = \{ \hat{\vec{x}}_s = \vec{x}_s(\vec{x}, t; t-s), \quad s \in [0, t] \} \quad . \quad (67)$$

Since the velocity vector is tangent to l , the pathline can be obtained by integrating the differential equation

$$\frac{d\vec{x}}{d\tau} = \vec{v}(\vec{x}_s, \tau) \quad , \quad (68)$$

with the initial condition $\hat{\vec{x}}_s(\vec{x}, t, \tau=t) = \vec{x}$.

In this work, this equation is solved thanks to the Euler integration scheme³² as illustrated in Fig. IV.10. This method allows one to reconstruct the pathline in the forward ($s < 0$) or the backward ($s > 0$) sense; i.e. from the position of the material point at the gate and the entry time to the last position at the end of the process, or

from the final position in the part, going back in time, to the entry of the particle into the mould.

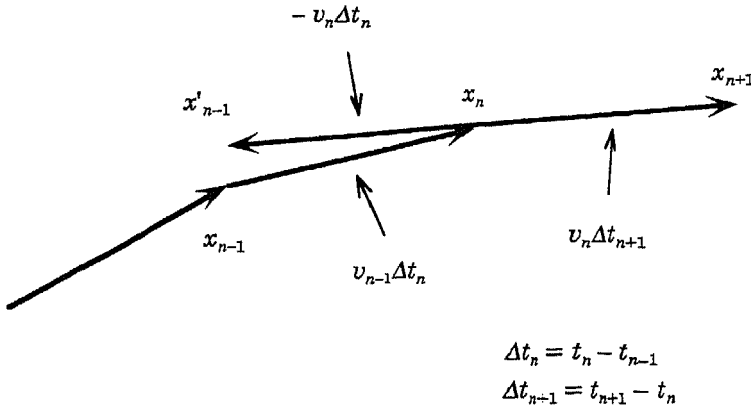


Figure IV.10 : Sketch of the tracking scheme.

Fountain flow is considered when the particle is leaving the flow domain, i.e. when its position is located outside of the temporary filled region delimited by the actual flow front. When such an event is encountered, the exact time at which fountain flow occurs is accurately determined by appropriate interpolation between the two successive flow fronts and the gapwise coordinate of the point is corrected using Eq. (40). The displacement of the material point and the interpolation for fountain flow is based on the knowledge, on the extrapolation mesh, of the 3D velocity field of the polymer and the velocity field of the flow front. However, as the front F_{n+1} does not match exactly the predetermined new front $\hat{F}_{n+1}$ a corrected extrapolation mesh must be built. The principle is illustrated in Fig. IV.11. Point x_{n+1} located in Γ_{n+1}^h is moving backward. As its velocity is not sufficient enough, its final location (x'_n) lies outside the mesh Γ_n^h . In fact, this point has experienced fountain flow during its displacement. As its velocity is lower than that of the front, it is possible to calculate the exact time at which the flow front reaches the point. At this time, the gapwise coordinate of the point is corrected thanks to Eq. (40). Being at a lower gapwise coordinate, it has a higher velocity, leading the point to be

localized in Γ_n^h . Details concerning the tracking algorithm may be found in Verhoyen³³.

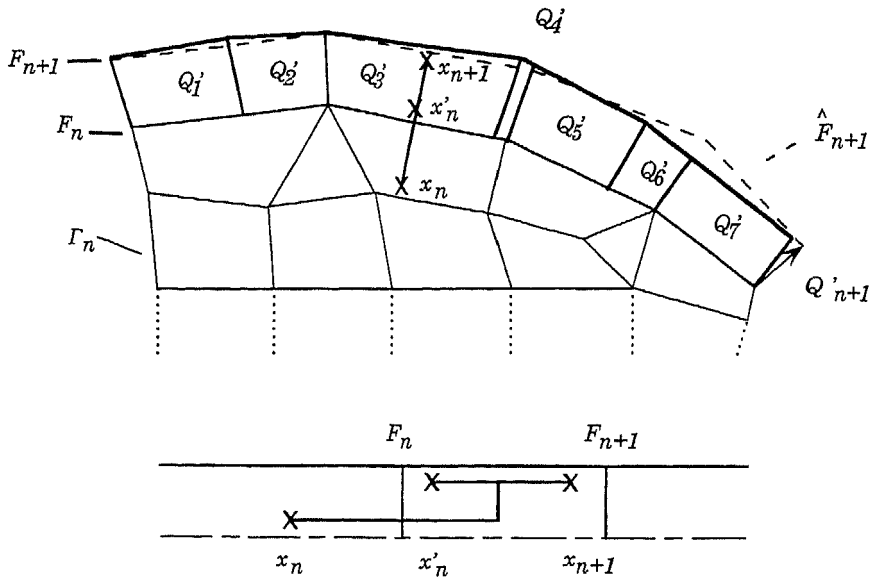


Figure IV.11 : Backward tracking of a material point. Sketch of the fountain flow effect.

6. Conclusions

We have presented in this chapter the principles of a general method for the numerical simulation of non-isothermal flow in injection moulding. Starting from continuum mechanics and introducing appropriate simplifying assumptions, a mathematical model of injection moulding has been presented. The numerical techniques required to solve the problem has been described, leading to the present version of the numerical simulation software *MOLDSYS*. As our objective is to simulate the moulding of semi-crystalline polymers, additional details related to flow calculations will be omitted. More information on the *MOLDSYS* code can be found in Dupret¹.

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Chapter V

A simplified method for introducing the Cross viscosity law in the numerical simulation of Hele Shaw flow

Abstract

The aim of this chapter is to analyse the influence of the polymer viscosity on its flow during the injection moulding process. A new method is developed in order to easily represent any viscosity law exhibiting a Newtonian plateau at a low shear rate, and a power-law dependence at a high shear rate. In particular, the Cross law can be used without involving a dramatic increase of the computational cost through multiple quadratures in the gapwise direction during pressure calculations. Several examples are analysed and discussed.

1. Introduction

The Hele-Shaw model is widely used for the simulation of injection and compression moulding¹⁻¹⁷. An important part of the published work is however based on using a power-law viscosity, since this provides a convenient way to factor out the pressure gradient contribution in the calculation of the fluidity (which represents the non-linear ratio between the local flow rate and the pressure gradient vectors). As the fluidity is the result of an integration in the gap-wise direction – which is required because injection and compression moulding processes typically exhibit three-dimensional temperature fields, which in turn give rise to a 3D viscosity –, factoring out the effect of pressure in the calculation of the fluidity is the only way to avoid to embed costly integrations in pressure iterations. A single integration in the gap-wise direction is therefore required per time step in order to solve for the pressure field when a power law viscosity is used.

Unfortunately, the power-law model is far from being satisfactory in many circumstances of practical interest. Indeed, industrial parts often feature complex shapes, with thicker and thinner regions, which do not allow for a power-law approximation of the viscosity because the wall shear rate range is too extended. An appropriate viscosity law must therefore be used to obtain accurate results.

Among several available viscosity models, the Carreau and especially the Cross laws must be retained in view of their excellent agreement with reality for many thermoplastic polymers of industrial interest¹⁸⁻²¹. The Cross viscosity law is the simpler one, with a Newtonian plateau at low shear rate and a power-law asymptote at high shear rate (in the log-log diagram). In addition, the Carreau law may show a second (and lower) viscosity plateau at high shear rate, which is however of lesser importance because of the very high shear rates which are necessary to reach the second plateau. We will therefore focus on the Cross law.

The objective of the present chapter is twofold. First, a general method is developed to approximate the Cross law by an accurate expansion that presents most of the numerical advantages of the power-law viscosity. Secondly, a theoretical analysis is carried out together with numerical experiments, in order to investigate

the effect of the viscosity law upon the flow behaviour during the filling stage of the moulding process. It is surprisingly found that, in some isothermal cases, the front pattern is totally independent of the viscosity law selection. This explains why the power-law viscosity model often brings on accurate kinematics, but poor pressure predictions. Numerical tests also demonstrate the importance of thermal effects, which can completely modify the front motion. As viscosities are in general strongly temperature dependent, one may conclude that an important indirect influence of the viscosity law upon the kinematics can be induced by thermal effects.

It is therefore clear that a computationally cheap method to integrate the Cross viscosity law in the simulation of the Hele-Shaw flows, such as found during the filling stage of injection and compression moulding, represents a numerical tool of particular interest. This method has permitted us, by use of the *MOLDSYS* simulation software^{12-17,22-26}, to investigate the filling of several parts. Calculated results largely confirm theoretical predictions concerning the impact of the viscosity law on the front pattern and the evolution of the pressure field in the part, together with the importance of thermal effects.

This chapter is subdivided as follows. The Hele-Shaw model is summarized in Section 2. Section 3 is devoted to developing the expansion that is used to approximate the Cross viscosity law in a cheap and accurate way. Isothermal and non-isothermal results are presented in Section 4, while a theoretical analysis is carried out on particular flows to explain why the front pattern is independent of the viscosity law in these cases. Conclusions are drawn in Section 5.

2. Modelling assumptions

The Hele-Shaw model¹⁻³ is appropriate to represent the flow of a generalized Newtonian fluid in a thin cavity. Assuming, for the sake of brevity, a constant gap thickness $2h$, and letting L represent a characteristic length of the part, this dimensional hypothesis is written as :

$$\varepsilon = \frac{h}{L} \ll 1 . \quad (1)$$

Asymptotic analysis allows one to simplify the governing field equations on this basis. In what follows, we will restrict ourselves to the case of an incompressible fluid, since extension of our method to the compressible case is straightforward. Under the lubrication approximation, the simplified mass, momentum and energy equations are written as :

$$\frac{\partial v_\alpha}{\partial x_\alpha} + \frac{\partial w}{\partial z} = 0 \quad , \quad (2)$$

$$\begin{cases} \frac{\partial p}{\partial x_\alpha} = \frac{\partial}{\partial z} \left(\eta \frac{\partial v_\alpha}{\partial z} \right) , \\ \frac{\partial p}{\partial z} = 0 \quad , \end{cases} \quad (3)$$

$$\rho c_p \left(\frac{\partial T}{\partial t} + v_\alpha \frac{\partial T}{\partial x_\alpha} + w \frac{\partial T}{\partial z} \right) = \frac{\partial}{\partial z} \left(k \frac{\partial T}{\partial z} \right) + \eta \dot{\gamma}^2 \quad , \quad (4)$$

where x_α and z stand for the in-plane and out-of-plane co-ordinates, respectively, p , T and (v_α, w) denote the pressure, temperature and velocity fields, and ρ , c_p , k , and η represent the fluid specific mass, specific heat, thermal conductivity and viscosity. The shear rate $\dot{\gamma}$ is approximated by the formula

$$\dot{\gamma}^2 = \frac{\partial v_\alpha}{\partial z} \frac{\partial v_\alpha}{\partial z} \quad . \quad (5)$$

Summation over repeated Greek indices (which take their values from 1 to 2) is assumed.

The advantage of the Hele-Shaw approach is to allow for averaging the mass equation over the thickness of the cavity, in order to get the equation governing the 2D pressure field. To this end, taking no-slip along the walls into account, in-plane velocity components are easily shown to be proportional to the pressure gradient,

$$v_\alpha = - \frac{\partial p}{\partial x_\alpha} \omega \quad , \quad (6)$$

where the profile function ω is defined as

$$\omega = \int_{-h}^h \frac{\xi}{\eta} d\xi \quad . \quad (7)$$

A second integration provides the gap-averaged velocity field $\bar{v}_\alpha$,

$$h \bar{v}_\alpha = - \frac{\partial p}{\partial x_\alpha} S_v, \quad (8)$$

where the fluidity S is calculated by integrating by part the profile function over the gap half-thickness :

$$S_v = \int_0^h \omega dz = \int_0^h \frac{z^2}{\eta} dz. \quad (9)$$

Finally, mass conservation yields the pressure equation :

$$\frac{\partial}{\partial x_\alpha} \left(S_v \frac{\partial p}{\partial x_\alpha} \right) = 0 \quad (10)$$

The system is closed, since the pressure and temperature fields are governed by Eqs. (10) and (4), while the velocity components and the shear rate can be obtained from Eqs. (6), (7), (2) and (5).

Several numerical schemes can be used to make this system discrete^{3,7,10-12,22}. In general, computer time can be saved by decoupling the temperature and pressure equations. In that case, a main difficulty is found in calculating the fluidity from Eq. (9), since the shear rate is highly dependent on the pressure gradient, and in turn has an important effect on the viscosity (in the non-Newtonian case). Hence, the decoupling strategy can be efficient only if the dependence of fluidity upon pressure gradient is taken into account in the mass equation (10). This can be easily achieved for a power-law viscosity^{3,4,12,22}. The aim of the present paper is to extend this approach to the Cross viscosity law.

3. Approximation of the Cross viscosity law

Using the Cross law (Fig. V.1), the viscosity η is expressed as :

$$\eta = \eta(T, p, \dot{\gamma}) = \frac{\eta_0}{1 + \left(\frac{\eta_0 \dot{\gamma}}{\tau_0} \right)^{1-n}}, \quad (11)$$

where the asymptotic power-index n is a constant,

$$0 < n < 1 , \quad (12)$$

while the viscosity at zero shear rate η_0 and the characteristic time τ_0 are assumed to be decoupled functions of pressure and temperature :

$$\eta_0 = \eta_0(T, p) = m_1(T) m_2(p) , \quad (13)$$

$$\tau_0 = \tau_0(T, p) = m_1^*(T) m_2^*(p) . \quad (14)$$

In practice, τ_0 is often supposed to be a constant.¹⁸

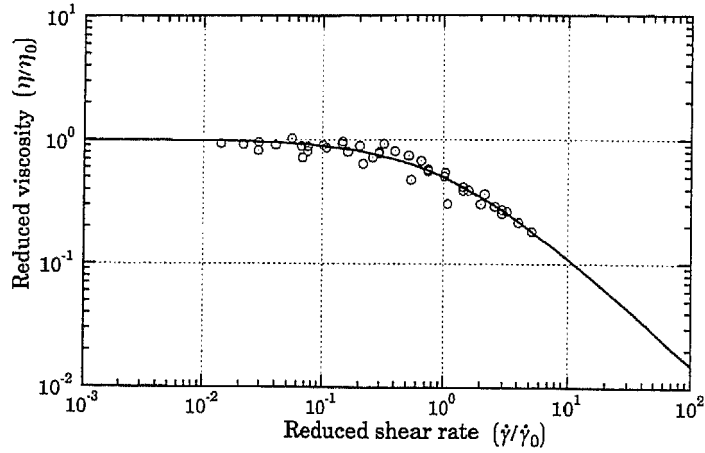


Figure V.1 : Experimental data ($\odot$) for a commercial-grade PC (Makrolon 2805) and corresponding best fit curve based on the Cross model. Experiments from Dupret.²⁷

The Cross law exhibits a Newtonian plateau at low shear rate,

$$\eta \sim \eta_0 , \quad \dot{\gamma} \rightarrow 0 , \quad (15)$$

and a power-law behaviour at high shear rate,

$$\eta \sim \hat{m}_1(T)^n \hat{m}_2(p)^n \dot{\gamma}^{n-1} , \quad \dot{\gamma} \rightarrow \infty , \quad (16)$$

with

$$\begin{aligned} \hat{m}_1(T) &= m_1(T) m_1^*(T)^{\frac{1}{n}-1} , \\ \hat{m}_2(p) &= m_2(p) m_2^*(p)^{\frac{1}{n}-1} . \end{aligned} \quad (17)$$

The classical Hele-Shaw theory is based on integrating the momentum equations in the z -direction and averaging the mass equation over the gap half-thickness. Letting Λ and τ denote the pressure gradient and the shear stress (which depends on z),

$$\Lambda = \left(\frac{\partial p}{\partial x_\alpha} \frac{\partial p}{\partial x_\alpha} \right)^{1/2}, \quad (18)$$

$$\tau = \eta \dot{\gamma}, \quad (19)$$

the momentum equation (3) are easily shown to involve the relation

$$\tau = \Lambda |z|, \quad (20)$$

or, equivalently,

$$\frac{z}{\eta} = \Lambda^{-1} \dot{\gamma} \quad (z \geq 0). \quad (21)$$

From Eqs. (7) and (9), the profile function and the fluidity are, therefore, given by the expressions

$$\omega = \Lambda^{-1} \int_z^h \dot{\gamma} d\zeta, \quad (22)$$

$$S_v = \Lambda^{-1} \int_0^h \dot{\gamma} |z| dz. \quad (23)$$

Consider now a power-law viscosity. From Eqs. (16) and (19), the shear stress is written as

$$\tau = (\hat{m}_1(T) \hat{m}_2(p) \dot{\gamma})^n, \quad (24)$$

from which it is easy to express the shear rate $\dot{\gamma}$ as a function of τ , p and T . Substituting $\Lambda |z|$ for τ from Eq. (20) in this latter relation, and using Eqs. (22) and (23), calculations yield the following expressions for the profile function and the fluidity :

$$\omega = \frac{\Lambda^{\frac{1}{n}-1}}{\hat{m}_2(p)} \int_z^h \frac{\zeta^{\frac{1}{n}}}{\hat{m}_1(T)} d\zeta, \quad (25)$$

$$S_v = \frac{\Lambda^{\frac{1}{n}-1}}{\hat{m}_2(p)} \int_0^h \frac{\zeta^{\frac{1}{n}+1}}{\hat{m}_1(T)} dz. \quad (26)$$

This approach is not possible in the case of the Cross law. Indeed, the dependence of shear stress with respect to shear rate takes, from Eqs. (11) and (19), the more complex form

$$\frac{\tau}{\tau_0} = F_n(\dot{\gamma}/\dot{\gamma}_0) = \frac{\dot{\gamma}/\dot{\gamma}_0}{1 + (\dot{\gamma}/\dot{\gamma}_0)^{1-n}} , \quad (27)$$

where the symbol $\dot{\gamma}_0$ is defined as follows :

$$\dot{\gamma}_0 = \frac{\tau_0}{\eta_0} . \quad (28)$$

The difficulty lies in the fact that the function F_n cannot explicitly be inverted.

Nevertheless, we can formally write

$$\frac{\dot{\gamma}}{\dot{\gamma}_0} = F_n^{-1}\left(\frac{\tau}{\tau_0}\right) = F_n^{-1}\left(\frac{A|z|}{\tau_0}\right) . \quad (29)$$

The following asymptotic behaviours are easy to show from Eqs. (15) and (16) :

– at low shear stress, a Newtonian viscosity plateau is observed :

$$\dot{\gamma}/\dot{\gamma}_0 \sim \tau/\tau_0 , \quad \tau \rightarrow 0 ; \quad (30)$$

– at high shear stress, a power-law viscosity is in effect :

$$\dot{\gamma}/\dot{\gamma}_0 \sim (\tau/\tau_0)^{1/n} , \quad \tau \rightarrow +\infty . \quad (31)$$

Hence, any approximation of F_n^{-1} by a sum of the form

$$\frac{\dot{\gamma}}{\dot{\gamma}_0} \approx \frac{\tau}{\tau_0} + \left(\frac{\tau}{\tau_0}\right)^{\frac{1}{n}} + \sum_{i=3}^m A_i \left(\frac{\tau}{\tau_0}\right)^{\frac{B_i}{n}} , \quad (32)$$

will keep the same asymptotes, provided coefficients B_i be located in the following range :

$$n < B_i < 1 , \quad (33)$$

while A_i are fitting coefficients.

Using such development (32) for $\dot{\gamma}$, and using again Eqs. (22) and (23), the profile function and the fluidity are approximated as :

$$\begin{aligned} \omega = & \frac{1}{m_2(p)} \int_z^h \frac{\zeta}{m_1(T)} d\zeta + \frac{\Lambda^{\frac{1}{n}-1}}{\bar{m}_2(p)} \int_z^h \frac{\zeta^{\frac{1}{n}}}{\bar{m}_1(T)} d\zeta \\ & + \sum_{i=3}^m A_i \frac{\Lambda^{\frac{B_i}{n}-1}}{\bar{m}_2^i(p)} \int_z^h \frac{\zeta^{\frac{B_i}{n}}}{\bar{m}_1^i(T)} d\zeta, \end{aligned} \quad (34)$$

$$\begin{aligned} S_v = & \frac{1}{m_2(p)} \int_0^h \frac{z^2}{m_1(T)} dz + \frac{\Lambda^{\frac{1}{n}-1}}{\bar{m}_2(p)} \int_0^h \frac{z^{\frac{1}{n}+1}}{\bar{m}_1(T)} dz \\ & + \sum_{i=3}^m A_i \frac{\Lambda^{\frac{B_i}{n}-1}}{\bar{m}_2^i(p)} \int_0^h \frac{z^{\frac{B_i}{n}+1}}{\bar{m}_1^i(T)} dz, \end{aligned} \quad (35)$$

where the functions $\bar{m}_1^i(T)$ and $\bar{m}_2^i(p)$ are defined as :

$$\begin{aligned} \bar{m}_1^i(T) &= m_1(T) m_1^*(T)^{\frac{B_i}{n}-1}, \\ \bar{m}_2^i(p) &= m_2(p) m_2^*(p)^{\frac{B_i}{n}-1}. \end{aligned} \quad (36)$$

The mass equation (10) takes thus a form that is suitable for decoupling pressure and temperature calculations, since all the integrals in Eq. (35) depend on the temperature profile only. A weak form of the mass equation (which governs the pressure field) can easily be obtained by multiplying this equation by a test function $p'(x_\alpha)$ and integrating the result by parts. Finite element Galerkin discretisations can be derived in this way^{3,10,11,22}.

It is worth noting that more complex representations of the viscosity at zero shear rate η_0 than in Eq. (13) can give rise to similar simplifications. Let indeed η_0^{-1} be defined by a sum of the following form :

$$\frac{1}{\eta_0} = \sum_k \frac{1}{m_{1k}(T) m_{2k}(p)}, \quad (37)$$

while τ_0 keeps the form (14). From Eqs. (28) and (32), one easily obtains the relation

$$\dot{\gamma} = \sum_k \left[\frac{\tau}{m_{1k}(T) m_{2k}(p)} + \frac{\tau^{1/n}}{\bar{m}_{1k}(T) \bar{m}_{2k}(p)} + \sum_{i=3}^m \frac{A_i \tau^{B_i/n}}{\bar{m}_{1k}^i(T) \bar{m}_{2k}^i(p)} \right], \quad (38)$$

where the functions $\bar{m}_{1k}(T)$, $\bar{m}_{2k}(p)$, $\bar{m}_{1k}^i(T)$ and $\bar{m}_{2k}^i(p)$ are defined from $m_{1k}(T)$, $m_{2k}(p)$, $m_1^*(T)$ and $m_2^*(p)$ as in Eqs. (17) and (36). The resulting profile function and fluidity are expressed in the same forms as in Eqs. (34) and (35), from which decoupled pressure and temperature calculations can again be performed.

4. Results and discussion

Material data (corresponding to the Makrolon 2805 Polycarbonate) are given in Table V.1.

Table V.1

Material data for the Makrolon 2805 Polycarbonate.

n	0.09275	
τ_0	$1.1614 \cdot 10^6$	[Pa]
η_0	$3 \cdot 10^8 \exp(-0.035 T)$ above T_g $\rightarrow \infty$ (see Dheur ²⁴) below T_g	[Pa s]
T_g	423	[K]
c_p	2200	[J / kg K]
k	0.215	[W / m K]
ρ	$1.2 \cdot 10^{-6}$	[kg / m ³]

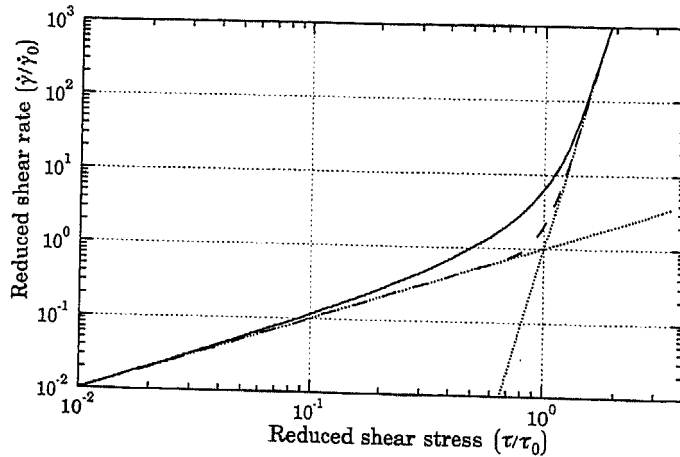


Figure V.2 : The function F_n^{-1} (—) and its approximation (— —) by a two term sum defined from its asymptotes.

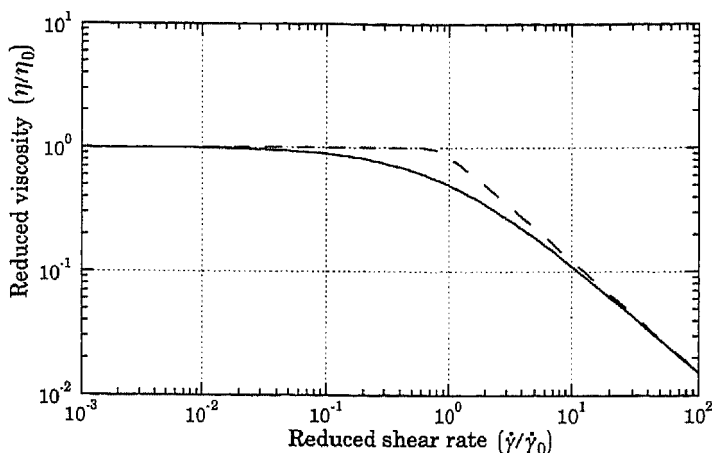


Figure V.3 : True reduced viscosity (—) as compared to the approximate reduced viscosity resulting from a two term representation of F_n^{-1} (---).

Numerical experiments show that approximating the function F_n^{-1} in Eqs. (29) and (32) by a two term sum ($m = 2$) gives rise to poor results (Figs. V.2 and V.3), while a three term approximation ($m = 3$), with $A_3 = 1.78$ and $B_3 = 0.23$, is much more accurate (Figs. V.4 and V.5). In view of the agreement between three terms approximation and exact function, additional terms are not useful while it will result in an increase of computational cost.

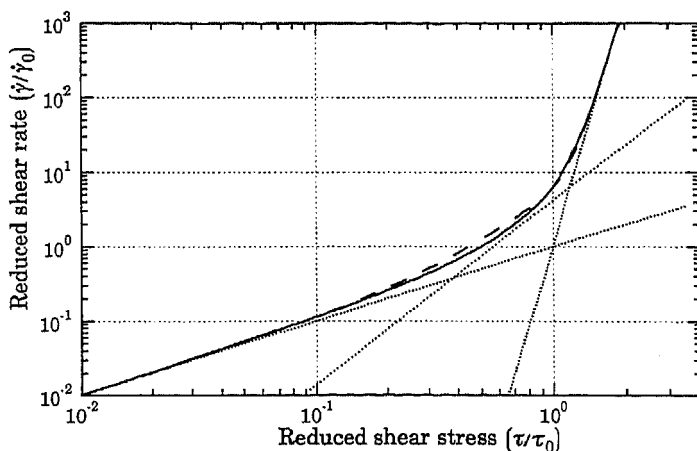


Figure V.4 : The function F_n^{-1} (—) and its approximation (---) by a three term sum defined from its asymptotes and an additional term.

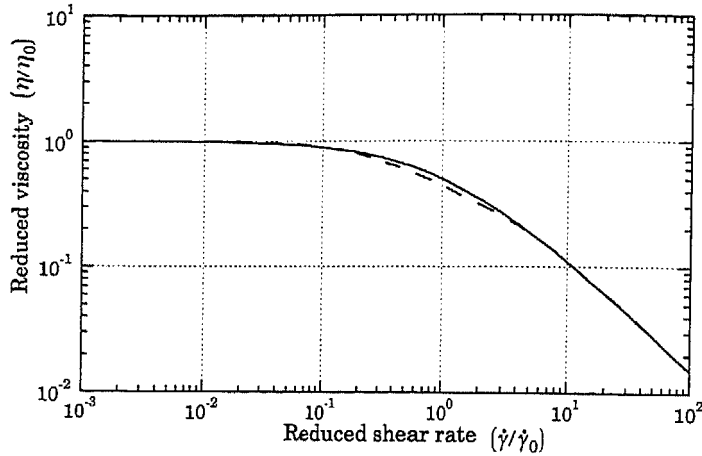


Figure V.5 : True reduced viscosity (—) as compared to the approximate reduced viscosity resulting from a three term representation of F_n^{-1} (---).

4.1. Isothermal simulations

A first set of examples deals with isothermal simulations. The viscosity at zero shear rate and characteristic time are thus constant. The material is injected at the fixed temperature of 573 K.

The 1D filling of a $120 \times 50 \times 2$ mm³ rectangular plate fed through a linear gate (Fig. V.6) is first considered at different flow rates. Figs. V.6 to V.8 depict the wall shear rate, final gate pressure and reduced velocity profile (i.e. the dimensionless ratio between the velocity profile and the average velocity in the gap) as functions of the flow rate, together with the associated asymptotic results. The transition from a Newtonian to a power law flow behaviour is clearly exhibited.

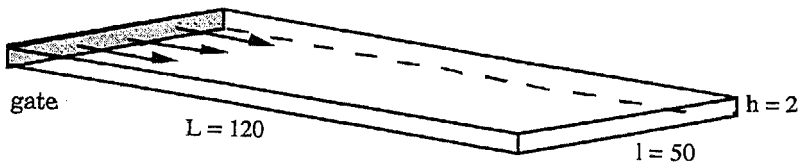


Figure V.6 : 1D filling of a rectangular plate..

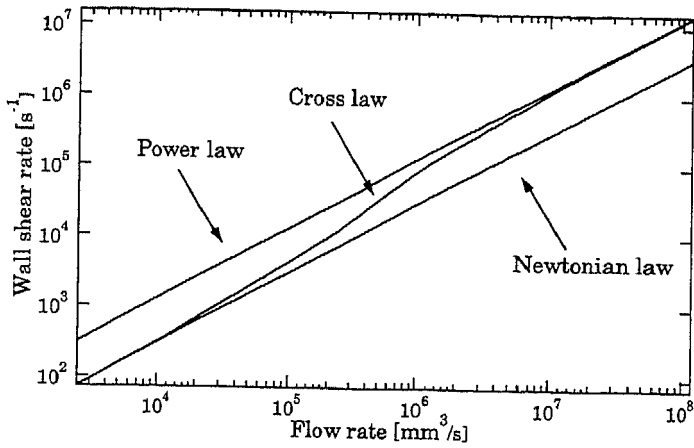


Figure V.7 : 1D filling of a rectangular plate. Wall shear rate as a function of the flow rate for a Newtonian, power law and Cross viscosity law.

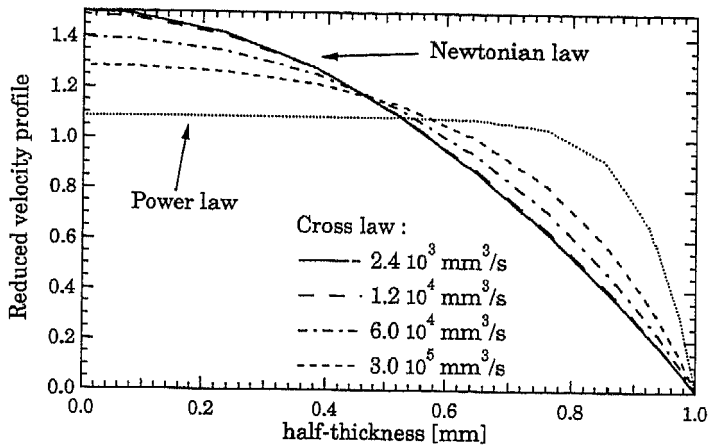


Figure V.8 : Same case as in Fig. 7. Gate pressure at the end of filling as a function of the flow rate for a Newtonian, power law and Cross viscosity law.

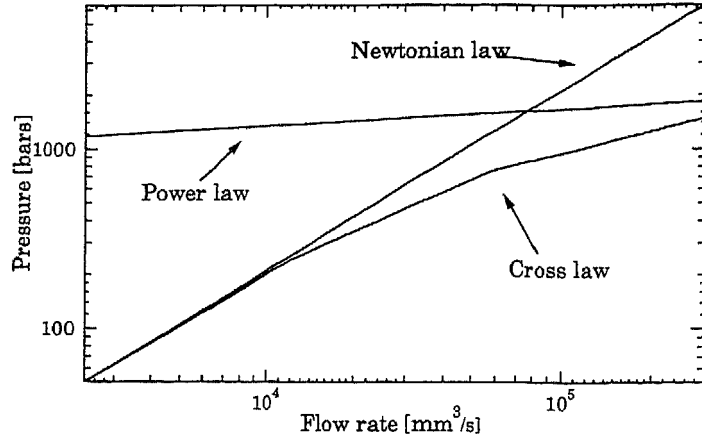


Figure V.9 : Same case as in Fig. 7. Reduced velocity profile as a function of the flow rate for a Newtonian, power law and Cross viscosity law.

In a second example (Fig. V.10), the isothermal filling of a part with two branches of different thickness is analysed. The total length of the part is 550 mm, while the thickness of the two branches and of the upstream thick rib is of 2 mm, 10 mm and 20 mm, respectively. The imposed flow rate is of $1.8 \cdot 10^5 \text{ mm}^3/\text{s}$.

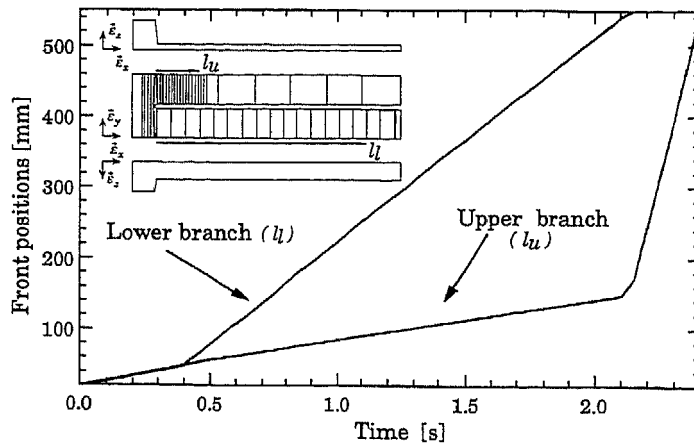


Figure V.10 : Isothermal filling of a part with two branches of different thickness. Front positions as functions of time.

Three steps can be identified, namely the filling of the upstream thick rib, the filling of the lower branch (during which the front moves slowly in the upper branch), and the end of the filling of the upper branch. In this example, such as in the following one, the successive positions of the flow fronts do not depend on the index n , nor on the parameters τ_0 and η_0 , nor on the flow rate (provided the time scale be adapted to the flow rate). This important result is a formal consequence of the simplified problem assumptions (i.e. isothermal flow, incompressible fluid, and constant η_0 and τ_0). Indeed, the first and third steps of the filling are governed by incompressibility, and it is thus sufficient to explain the motion of the flow fronts during the second step. Consider a given time t , and let l_u and l_l denote the horizontal distances between the branching location and the upper and lower front, respectively (see Fig. V.9), while S_u , S_l , $\bar{v}_{lu}$ and $\bar{v}_{ll}$ stand for the upper and lower fluidities and average velocities, h_u and h_l are the branch thicknesses, t_0 is the time at which the flow front separates in two branches, and W_0 is the pressure increase per unit time at the separation location. Assuming constant S_u , S_l , $\bar{v}_{lu}$, $\bar{v}_{ll}$ and W_0 during the second step of the filling, Eq. (8) is written as :

$$\begin{aligned} h_u \bar{v}_{lu} &= S_u W_0 (t - t_0) / l_u , \\ h_l \bar{v}_{ll} &= S_l W_0 (t - t_0) / l_l , \end{aligned} \quad (39)$$

from which the following relations are easily obtained :

$$\begin{aligned} h_u \bar{v}_{lu}^2 &= S_u W_0 , \\ h_l \bar{v}_{ll}^2 &= S_l W_0 , \end{aligned} \quad (40)$$

since $l_u = \bar{v}_{lu} (t - t_0)$ and $l_l = \bar{v}_{ll} (t - t_0)$. On the other hand, fluidities are given by Eqs. (23) and (29) (or its approximation (35)) :

$$\begin{aligned} S_u &= \bar{v}_{lu}^2 \frac{\tau_0^2 h_u}{W_0^2 \eta_0} H_n \left(\frac{h_u W_0}{\tau_0 \bar{v}_{lu}} \right) , \\ S_l &= \bar{v}_{ll}^2 \frac{\tau_0^2 h_l}{W_0^2 \eta_0} H_n \left(\frac{h_l W_0}{\tau_0 \bar{v}_{ll}} \right) , \end{aligned} \quad (41)$$

where $H_n(\xi)$ is the average

$$H_n(\xi) = \frac{1}{\xi} \int_0^\xi F_n^{-1}(\xi) \xi \, d\xi . \quad (42)$$

Eliminating S_u and S_l from Eqs. (40) and (41), one obtains the relations

$$\begin{aligned} H_n \left(\frac{h_u W_0}{\tau_0 \bar{v}_{1u}} \right) &= \frac{\eta_0 W_0}{\tau_0^2} , \\ H_n \left(\frac{h_l W_0}{\tau_0 \bar{v}_{1l}} \right) &= \frac{\eta_0 W_0}{\tau_0^2} , \end{aligned} \quad (43)$$

which immediately show that

$$\frac{\bar{v}_{1u}}{h_u} = \frac{\bar{v}_{1l}}{h_l} , \quad (44)$$

since $H_n(\zeta)$ is a strictly increasing function. Hence, average velocities during the second step of the filling are proportional to the upper and lower gap thicknesses, which shows that successive front positions depend on the total flow rate only.

The third example, which concerns the filling of a 550 mm $\times$ 190 mm plate of variable thickness (Fig. V.11) at a $4 \cdot 10^6$ mm³/s flow rate, gives rise to similar conclusions. The upstream rib is 20 mm thick, while the upper and lower downstream thicknesses are of 2 mm and 10 mm respectively.

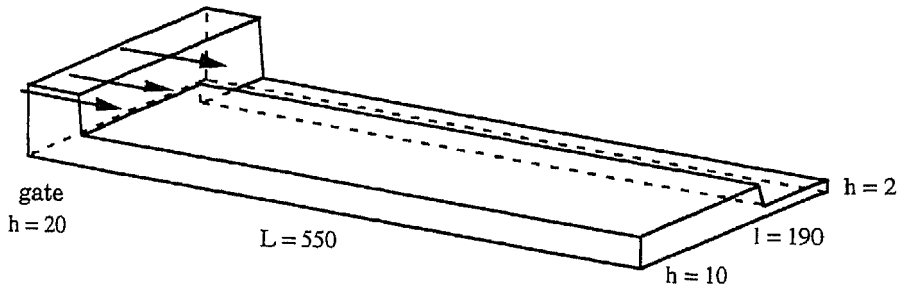


Figure V.11 : Scheme of the variable thickness plate.

A theoretical analysis of the front behaviour can be carried out by considering the developed flow in an infinite plate, with an abrupt change of thickness separating an upper and lower region. Letting the symbols h_u , $(\bar{v}_{1u}, \bar{v}_{2u})$, S_u , $(\Lambda_1, \Lambda_{2u})$, Λ_u , and h_l , $(\bar{v}_{1l}, \bar{v}_{2l})$, S_l , $(\Lambda_1, \Lambda_{2l})$, Λ_l , denote the upper and lower thickness, velocity, fluidity, pressure gradient and pressure gradient norm, respectively, relations (8) take the form

$$\begin{cases} h_u \bar{v}_{1u} = S_u \Lambda_1 , \\ h_l \bar{v}_{1l} = S_l \Lambda_1 , \end{cases} \quad (45)$$

$$\begin{cases} h_u \bar{v}_{2u} = S_u \Lambda_{2u} , \\ h_l \bar{v}_{2l} = S_l \Lambda_{2l} , \end{cases} \quad (46)$$

while, from Eqs. (23), (29) and (42), fluidities are given by the expressions

$$\begin{cases} S_u = \frac{\tau_0^2 h_u}{\eta_0 \Lambda_u^2} H_n \left(\frac{h_u \Lambda_u}{\tau_0} \right) , \\ S_l = \frac{\tau_0^2 h_l}{\eta_0 \Lambda_l^2} H_n \left(\frac{h_l \Lambda_l}{\tau_0} \right) . \end{cases} \quad (47)$$

According to the theory developed by Couniot *et al.*¹³, the pressure gradient component Λ_1 along the abrupt change of thickness is the same in the upper and lower region. On the other hand, mass conservation yields the equation

$$h_u \bar{v}_{2u} = h_l \bar{v}_{2l} , \quad (48)$$

while the uniqueness of the front velocity $\bar{v}_f$ along the change of thickness line (Fig. V.12) yields the relation

$$\frac{\bar{v}_{1u}^2 + \bar{v}_{2u}^2}{\bar{v}_{1u}} = \frac{\bar{v}_{1l}^2 + \bar{v}_{2l}^2}{\bar{v}_{1l}} = \bar{v}_f . \quad (49)$$

Keeping in mind the present model hypothesis of homogeneous upper and lower flows, it should be noted that Eqs. (49) are, in the general case, valid at the flow front only.

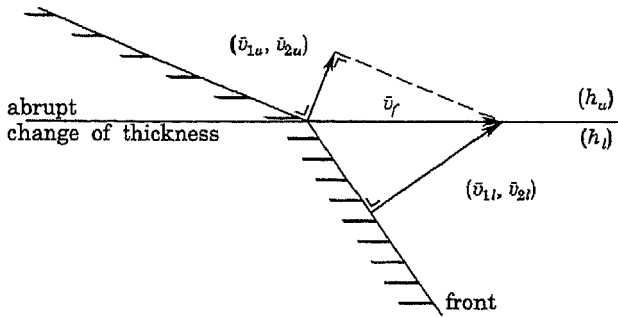


Figure V.12 : Front velocity diagram for an abrupt change of thickness.

The key point is to observe that, under the isothermal assumption, velocities and gap thicknesses are related by the equation

$$\frac{\bar{v}_{1u}}{\bar{v}_{1l}} = \frac{h_u^2}{h_l^2} . \quad (50)$$

Indeed, calculating Λ_u^2 and Λ_l^2 from Eqs. (45) and (46), and using Eq. (49), one easily obtains the relation

$$\frac{\Lambda_u^2}{\Lambda_l^2} = \frac{h_u^2 S_l^2}{h_l^2 S_u^2} \frac{\bar{v}_{1u}}{\bar{v}_{1l}} , \quad (51)$$

from which, using again Eq. (45), it results that

$$\frac{\Lambda_u^2 S_u}{\Lambda_l^2 S_l} = \frac{h_u}{h_l} . \quad (52)$$

As, on the other hand, Eqs. (47) yield the relation

$$\frac{\Lambda_u^2 S_u}{\Lambda_l^2 S_l} = \frac{h_u H_n(h_u \Lambda_u / \tau_0)}{h_l H_n(h_l \Lambda_l / \tau_0)} , \quad (53)$$

it becomes obvious that

$$h_u \Lambda_u = h_l \Lambda_l , \quad (54)$$

since again $H_n(\xi)$ is a strictly increasing function. From Eqs. (52) and (54), it can also be shown that

$$S_u \Lambda_u^3 = S_l \Lambda_l^3 , \quad (55)$$

$$\text{and} \quad \frac{S_u}{h_u^3} = \frac{S_l}{h_l^3} , \quad (56)$$

from which Eq. (50) is easily deduced by use of Eq. (45).

Equations (48), (49) and (50) form a system from which the four dimensionless velocity components $\bar{v}_{1u}/\bar{v}_f$, $\bar{v}_{1l}/\bar{v}_f$, $\bar{v}_{2u}/\bar{v}_f$ and $\bar{v}_{2l}/\bar{v}_f$ can easily be determined as functions of the thickness ratio h_u/h_l . This shows that the front slope is a function of the thickness ratio only in isothermal flow, which is clearly observed in Fig. V.11. This result, together with the previous simulation (Fig. V.9), explains why, in many circumstances, the front pattern is not highly influenced by the viscosity dependence upon shear rate.

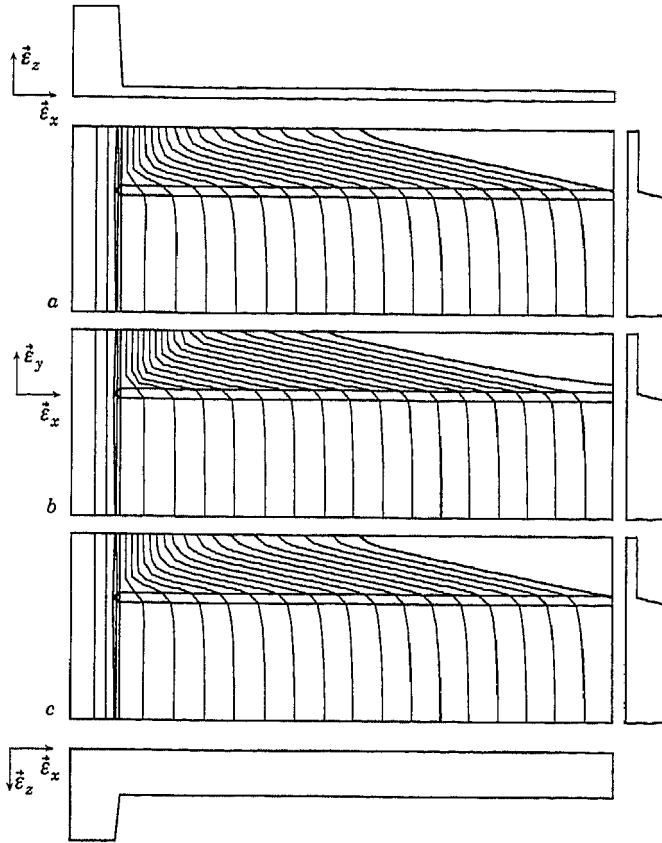


Figure V.13 : Isothermal filling of a plate of variable thickness. Front pattern for a Newtonian fluid (a), a power-law fluid (b), and a Cross fluid (c).

The fourth and fifth examples are devoted to illustrating isothermal situations where a slight effect of the viscosity law upon the front motion is observed. First, in Fig. V.14, the filling of a part with two different branches of varying thickness is analysed. The imposed flow rate is $1.8 \cdot 10^5 \text{ mm}^3/\text{s}$. The quasi-abrupt change of thickness clearly induces a dependence of the front motion with respect to the viscosity law. No self-similarity is indeed present in the solution after completion of the filling of the first (left) half of the lower branch. This means that, expressing the upper and lower fluidities by means of the function H_n as in Eqs. (41) and (47), the argument of this function is no longer the same in the whole part during the filling of the second (right) half of the lower branch.

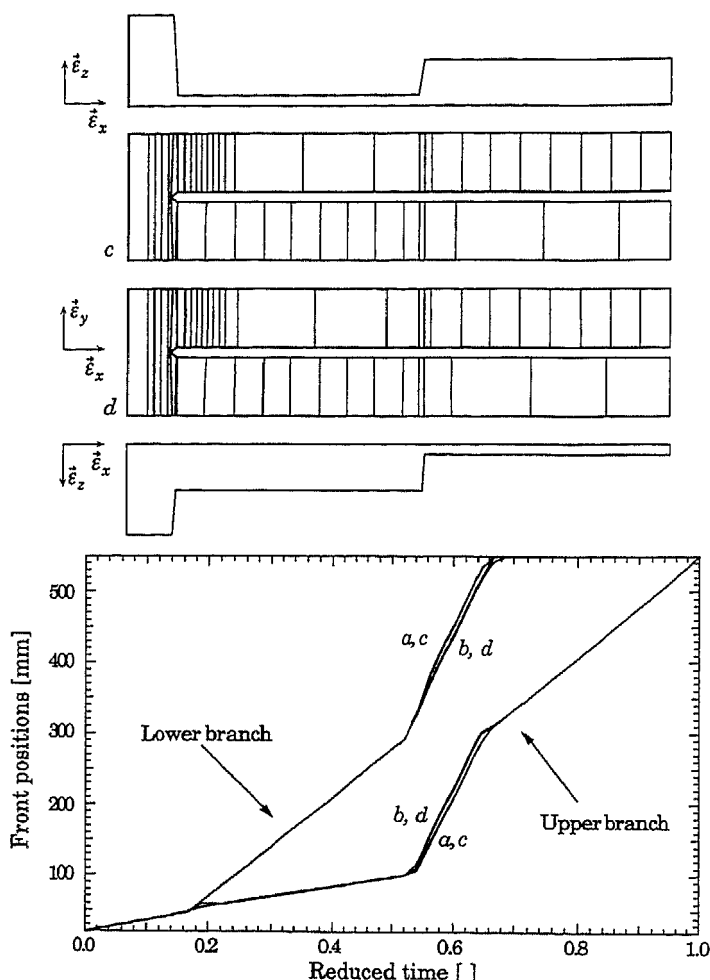


Figure V.14 : Isothermal filling of a part with two branches of varying thickness. Front positions as functions of time : (a) Newtonian fluid; (b) power-law viscosity; (c) Cross viscosity law; (d) Cross viscosity law, 100 times higher flow rate.

In the present case, due to the relatively low value of the imposed flow rate, the behaviour of the Cross viscosity fluid is close to Newtonian. Multiplying the flow rate by a factor of 100 however switches the flow to a power-law pattern.

The same phenomenon can be observed in Figs. V.15 and V.16, which concern the isothermal filling of a 550 mm $\times$ 130 mm part, whose thickness varies linearly in

the transverse direction from 0.5 to 10 mm after a thick rib of 20 mm. The imposed flow rate is $2 \cdot 10^5 \text{ mm}^3/\text{s}$. The difference between Newtonian and power-law front patterns is clearly more pronounced near the thin side of the part. Again, using a Cross viscosity-law switches the developed front shape from Newtonian to power-law when the flow rate is multiplied by a factor of 1000. Pressures are on the other hand highly dependent upon viscosity.

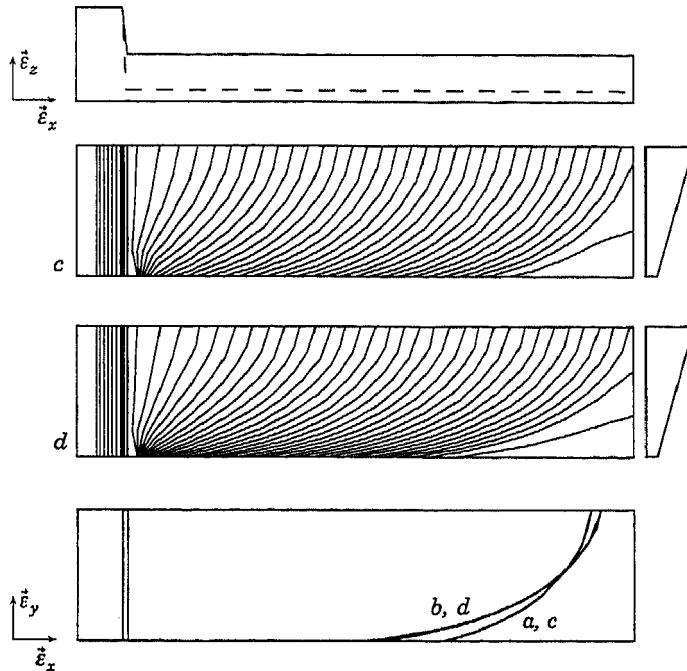


Figure V.15 : Isothermal filling of a part of linearly varying thickness. Successive front positions and developed front patterns : (a) Newtonian fluid; (b) power-law viscosity; (c) Cross viscosity law; (d) Cross viscosity law, 1000 times higher flow rate.

4.2. Non-isothermal simulations

A last example deals with non-isothermal effects. The filled part is the same plate of linearly varying thickness as in the 5th case of Section 4.1 (Figs. V.15 and V.16). The inlet temperature is 573 K while the initial wall temperature is 373 K.

Thermal boundary conditions are imposed using the concept of heat penetration inside the wall developed by Mal *et al.*²⁸

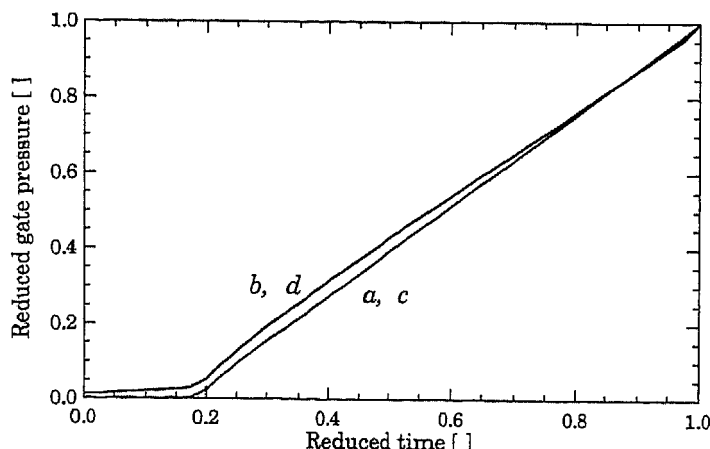


Figure V.16 : Same cases as in Fig. 15. Evolution of the gate pressure : (a) Newtonian fluid; (b) power-law viscosity; (c) Cross viscosity law; (d) Cross viscosity law, 1000 times higher flow rate.

Several cases have been analysed. Two reference simulations were first performed at a $0.4 \cdot 10^5$ and $2 \cdot 10^5 \text{ mm}^3/\text{s}$ flow rate, using the asymptotic Newtonian and power-law viscosities associated with the selected polycarbonate (see Table 1). It was impossible to complete the highest flow rate test with a power-law viscosity, since viscous heating in the thickest upper zone was too important leading to numerical instabilities. Simulations with the Cross viscosity law were subsequently performed at the same flow rates, in order to illustrate the progressive switch from Newtonian to power-law behaviour. It must however be emphasised that this situation is quite complex, since the velocity profile does not correspond to the same equivalent power index in the whole part.

Basically, the results shown in Fig. 17 exhibit the same phenomenon as discussed by Dheur *et al.*²⁹. Viscous heating is more important in the thicker zone, due to a much higher average velocity than in the thin zone (where cooling down is more pronounced). Thermal effects therefore tend to amplify the influence of the varying thickness. This amplification is however lower with the Cross law than with

the asymptotic power-law viscosity, which effect is sufficient to keep viscous heating at a quite reasonable level. Moreover, comparing the successive flow fronts in Figs 13 and 15, it should be observed that thermal effects have a deeper impact on the front shape than the viscosity law. In general, selecting an accurate dependence of the viscosity with respect to shear rate, such as involved by the Cross law, is more important for improving the quality of the pressure field than for the front pattern. Thermal effects always play a complex and important role in a large range of process operating data.

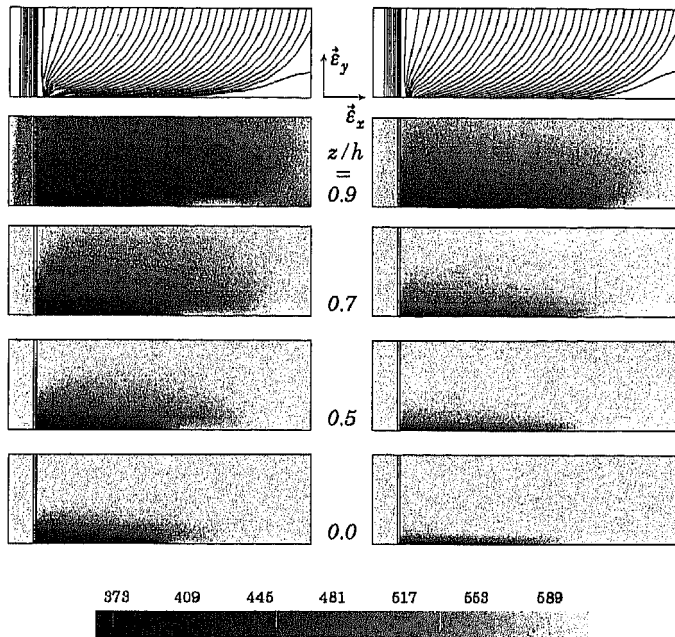


Figure V.17 : Same problem as in Fig. 15. Non-isothermal simulation for a Cross fluid. Successive flow fronts and layer by layer temperature field (from midplane ($z/h=0$) near to the wall $z/h=0.9$). Left : flow rate = $0.4 \cdot 10^5 \text{ mm}^3/\text{s}$; right : flow rate = $2 \cdot 10^5 \text{ mm}^3/\text{s}$.

5. Conclusions

We have presented a numerical method to simulate the Hele-Shaw flow of thermoplastic polymers governed by the Cross viscosity law, by means of decoupled pressure and temperature calculations. The scheme is based on a suitable expansion of the reduced shear rate in terms of the reduced shear stress (see Eqs. (29) and (32)), which keeps the correct asymptotes of this expression. While thermal calculations are exactly the same with this approach as with the classical Hele-Shaw simulations, pressure calculations are almost the same, the only difference being that the number of integrations in the gap-wise direction is multiplied by a factor of 3.

Analysis of theoretical and simulated results has shown that the viscosity dependence with respect to shear rate has a reduced influence upon the front pattern, which might even be completely absent in some isothermal flows due to self-similarity of the solution. The effect of the viscosity law can however be enhanced by thermal effects. On the other hand, the pressure field is always highly dependent on the viscosity law, which justifies to introduce complex laws in the numerical model.

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