

Multiscale Modeling of Polymer Crystallization

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Abstract: The crystallization process during filling and cooling in an injection molding process is investigated. The numerical methods, crystallization models and their implementation into a simulation chain with COMSOL and SphäroSim software are described.

Keywords: Polymer, Crystallization, Computer Simulation.

1. Introduction

The manufacturing of high quality injection molded parts requires a deep understanding of material properties, process parameters and product design. The behavior of a polymer during the injection molding process and the performance of the final part are significantly influenced by the microstructure formed during filling and cooling. During processing, a polymer is normally subject to a complex thermo-mechanical history that leads to different microstructures at different locations, because of variations in shear rate, pressure and temperature. The prediction of the final microstructure is very important to attain manufacturing processes in which defects such as uncontrolled warpage, incorrect part dimensions, excessive weight, etc. are absent.

Predicting the microstructure requires the simulation of the crystallization process which is a complex problem because it is necessary to combine transport phenomena of the multi-phase flow in non-isothermal conditions with crystallization kinetics. This requires the calculation of polymer properties on a microscopic scale using information from a macroscopic scale (Figure 1). It is possible to define this problem as a multiscale materials design problem.

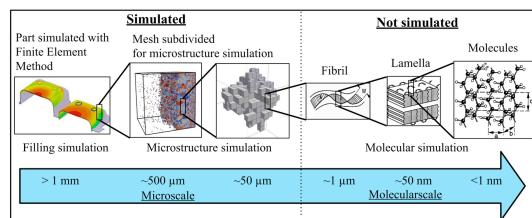


Figure 1. Macro-Micro level

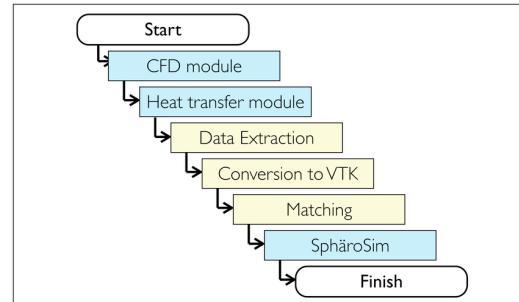


Figure 2. Module flowchart

The main objective of the presented work is to describe the crystallization kinetics of semi-crystalline thermoplastics with a multiscale model implemented into the COMSOL software and the in-house developed code SphäroSim (*Hopmann et al.* [1]). This is done by identifying the analytical parameters needed to connect crystallization kinetics with molecular material properties and applying the analytical scheme to the numerical simulation during filling and cooling in an injection molding process.

2. Framework

The filling and cooling simulations, implemented by using the computational fluid dynamics (CFD) and heat transfer (HT) modules of COMSOL, require the simultaneous solution of non-Newtonian multi-phase flow (polymer/air) and thermal fields in non-isothermal condition and transient regime. The simulation results are collected, converted into the OpenSource file format VTK (Visualization Toolkit) and transferred to the SphäroSim code, after a matching operation with the COMSOL mesh. The SphäroSim code uses COMSOL results as input data to compute crystallization kinetics, using the COMSOL data as boundary conditions in the microstructure simulation. This allows the time resolved calculation of the crystallization process and a prediction of the final microstructure in the part which can be used in further simulations such as a structural analysis. The module flowchart is shown in Figure 2.

The computational modeling of polymer flow considers the 2D compressible Navier-

Stokes equations written in a strong conservation form for mass and momentum. Finding the solution of the governing equations is difficult using traditional analytical techniques which involve complex fluid-material interaction and non-Newtonian viscosity. Thus the CFD technique is applied here to compute the polymer flow in a specific section of the injection molded part. An uniform finite element grid is generated from the model geometry to assure a stable convergence rate. Parameters such as velocity, pressure, temperature and wall shear stress are computed.

The simulation of the crystallization kinetics is performed with the in-house developed microstructure simulation tool SphäroSim. The results from COMSOL are converted into the OpenSource file format VTK using hexaeder elements. The temperature and velocity in the nodes are transferred to SphäroSim where they are used as boundary conditions for the simulation of the crystallization process. Additionally a scalar value representing the position of the polymer-air interface is transferred to identify the proceeding of the flow front.

3. Governing Equations and Boundaries

The numerical model implements the solution of the non-isothermal flow problem and the crystallization evolution. The governing equations and boundary conditions are reported in the following paragraphs.

3.1 Non isothermal CFD

The solution of the fluid dynamics problem is a velocity vector field and fluid properties in the physical domain, normally coincident with the part geometry Ω . The main equations to solve are the continuity and momentum equations:

$$\frac{\partial \rho}{\partial t} + \nabla \rho \cdot \mathbf{u} = 0 \quad (1)$$

$$\frac{\partial \rho \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \rho \mathbf{u} = -\nabla p + \nabla \cdot \boldsymbol{\tau} + \mathbf{F} \quad (2)$$

where ρ is the density, \mathbf{u} the velocity field, p the pressure, $\boldsymbol{\tau}$ the viscous stress tensor and \mathbf{F} the sum of the external forces. The main variable of the computation are functions of time t and position (x,y,z) . For a 2D problem, the velocity vector \mathbf{u} is split into its components u and v , the viscous stress tensor matrix $\boldsymbol{\tau}$ into τ_x and τ_y . The relation between $\boldsymbol{\tau}$ and \mathbf{u} for a non-newtonian fluid is

$$\boldsymbol{\tau} = \mu \left[\nabla \mathbf{u} + (\nabla \mathbf{u})^T \right] - \frac{2}{3} \mu (\nabla \cdot \mathbf{u}) \mathbf{I} \quad (3)$$

with μ the viscosity. The problem to be solved is also non-isothermal and the equation of heat

transfer is

$$\rho C_p \left(\frac{\partial T}{\partial t} + \mathbf{u} \cdot \nabla T \right) = \nabla \cdot (k \nabla T) + Q \quad (4)$$

where C_p is the specific heat capacity, k is the thermal conductivity and Q contains heat sources other than viscous heating.

The system of equations is completed with the equations related to the multiphase flow. In this case the geometry consist of union of multi domains Ω_i , one for each fluid. The basic idea is the definition of the interface as a smooth scalar value ϕ which represents the mutual distance between the two fluids. For $\phi > 0.5$ the cell is filled with polymer melt, for $\phi < 0.5$ it is filled with air while $\phi = 0.5$ locates the interface between the two fluids. The interface position reads

$$\frac{\partial \phi}{\partial t} + \mathbf{u} \cdot \nabla \phi = f(\phi) \quad (5)$$

with the function $f(\phi)$ reported by [Yue et al.](#) [2]. In our case, the first fluid is the air whereas the other fluid is the polymer melt. The air is modeled as an ideal gas. The material properties of the two fluids and the interface position ϕ , read

$$\rho = \rho_{polymer} \cdot \phi + \rho_{air} \cdot (1-\phi) \quad (6)$$

$$C_p = C_{p,polymer} \cdot \phi + C_{p,air} \cdot (1-\phi) \quad (7)$$

$$k = k_{polymer} \cdot \phi + k_{air} \cdot (1-\phi) \quad (8)$$

$$\mu = \mu_{polymer} \cdot \phi + \mu_{air} \cdot (1-\phi) \quad (9)$$

The density of the polymer is implemented by using the modified 2-domain Tait equation ([Wang](#) [3])

$$\rho_{polymer} = \left\{ v_0 \left[1 - C \ln \left(1 + \frac{P}{B} \right) \right] + v_t \right\}^{-1} \quad (10)$$

where v_0 equals the specific volume at zero gauge, v_t is the specific volume decreases due to crystallization, B is the pressure sensitivity, C is universal constant equal to 0.894. The density of the air, considered as an ideal gas, is

$$\rho_{air} = p M \cdot (RT)^{-1} \quad (11)$$

where p is the pressure, M the molar mass, R the perfect gas constant and T the temperature.

The viscosity of air depends mostly on the temperature while the viscosity of the polymer varies according to the Cross-WLF model

$$\mu_{polymer} = \mu_0 \cdot \left[1 + \left(\lambda \dot{\gamma} / \tau^* \right)^{1-n} \right]^{-1} \quad (12)$$

where μ_0 is the zero shear viscosity in which the viscosity approaches a constant value at very low shear rates, $\partial\gamma/\partial t$ the shear rate, τ^* the critical stress level at the transition to shear thinning and n is the power law index in the high shear rate

regime. The zero shear viscosity μ_0 reads:

$$\mu_0 = D_1 \cdot e^{(-A_1(T-263.15)/(A_2+T-51.6))} \quad (13)$$

with A_1 , A_2 and D_1 material constants.

3.2 Crystallization

The simulation of the crystallization process starts, as soon as the nodes of the hexaeder mesh, transferred from COMSOL, are covered with melt. This is done by checking the value of ϕ in each node, which must be greater than 0.5. The crystallization is simulated using a cellular automaton in the software SphäroSim for which the hexaeder mesh is subdivided into a high resolution mesh. Each element of the high resolution mesh represents the phase state of a small volume in the simulation area. The phase state will be ‘solid’ if the element is part of a crystalline superstructure otherwise it is ‘melt’. The nucleation process is modeled using the Lauritzen and Hoffman approach ([Lauritzen and Hoffman](#) [4])

$$\dot{N} = CkT \Delta G \exp\left(-\frac{E_a}{kT}\right) \exp\left(-\frac{K_n}{T(\Delta G)^n}\right) \quad (14)$$

with C and K_n as material constants, k the Boltzmann constant, T the temperature, ΔG the free Energy and E_a an activation energy of the supercooled liquid-nucleus interface. The exponent n can assume the values 1 or 2 depending on the temperature region in which the homogenous nucleation takes place. The free energy is assumed to be the sum of a quiescent and a flow-induced term ([Acienro et. al.](#) [5])

$$\Delta G = \Delta G_q + \Delta G_f \quad (15)$$

Assuming that the nuclei are created because of a folding process of the polymers the quiescent part of the free energy can be modeled by

$$\Delta G_q = \Delta H_0 \left(1 - \frac{T}{T_{m0}}\right) \quad (16)$$

with the thermodynamic melting temperature T_{m0} and ΔH_0 the latent heat of fusion. The flow-induced part ΔG_f is computed using the reptation theory by [Doi and Edwards](#) [6] and the model proposed by [Marrucci and Grizzuti](#) [7]

$$\Delta G_f = \frac{3}{4\pi} ckT \int_{-\infty}^t [\psi(t,t') (\int \ln |E(t,t') \cdot u| du)] dt' \quad (17)$$

with c the volumetric concentration of primitive chain segments, ψ the Doi-Edwards memory function and E the deformation tensor between times t and t' . Using the nucleation model $\partial N / \partial t$ the number of nuclei, for each element of the high resolution mesh, are computed in

SphäroSim. As soon as a nucleus appears in an element the growing process of a crystalline superstructure is simulated by using the [Hoffman, Davis and Lauritzen](#) [8] model

$$G = G_0 \exp\left(-\frac{U^*}{R(T-T_\infty)}\right) \exp\left(-\frac{\kappa_G T_{m0}^2 (T_{m0}+T)}{2T^2(T_{m0}-T)}\right) \quad (18)$$

with U^* describing the activation energy for a chain segment to attach to the crystal, T_∞ the temperature of zero movement of the polymer chains and G_0 , κ_G as material constants. Each element of the high resolution mesh, which is fully covered by a growth front of a crystalline superstructure, changes the phase state from melt to solid.

3.4 Boundary Conditions

The Navier-Stokes equations can be solved by defining the boundary conditions for the part geometry, inlet, outlet and initial interface. These conditions are necessary because a tentative velocity can be found everywhere in the interior of the domain, except at the boundaries.

Concerning the mold/melt interface, the no-slip condition (described by $\mathbf{u} = 0$) is applied to the entire geometry, except inlet and outlet. This ensures that there is no flow across the wall boundary and the melt is not slipping along the wall.

The inlet (outlet) boundary is used to define the flow into (or out of) the geometry. A velocity profile is used to define the normal velocity into the geometry, with

$$\mathbf{u} = -\mathbf{n}u_t \quad (14)$$

where \mathbf{n} is a normal vector pointing out of the geometry and the velocity u_t is a function of time

$$u_t \text{ for } 0 \leq t < t_{ch} = u_{init} + (u_{stat} - u_{init}) \cdot \frac{t}{t_{change}} \quad (15)$$

$$u_t \text{ for } t_{ch} \leq t < t_{stat} = u_{stat} \quad (16)$$

$$u_t \text{ for } t_{stat} \leq t < t_{switch} = u_{stat} + (u_{stat} - u_{hold}) \cdot \frac{t - t_{switch}}{t_{fill} - t_{switch}} \quad (17)$$

$$u_t \text{ for } t_{switch} \leq t < t_{hold} = u_{hold} \quad (18)$$

where t_{change} , t_{switch} , t_{fill} and t_{hold} are times related to the change between initial and stationary velocity, to the switch between filling and holding, to the end of filling and to holding time. In addition u_{init} equals the initial velocity and u_{stat} the stationary velocity

$$u_{stat} = \dot{Q} / S_{in} \quad (19)$$

where $\partial Q / \partial t$ is the injection flow rate, S_{in} the inlet section and u_{hold} the holding velocity. [Figure 3](#) shows the resulting injection profile.

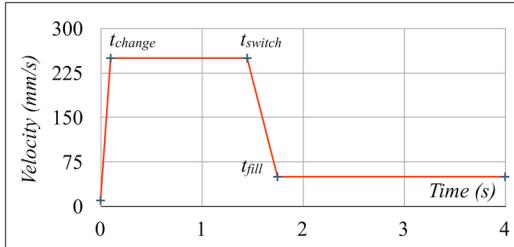


Figure 3. Injection profile

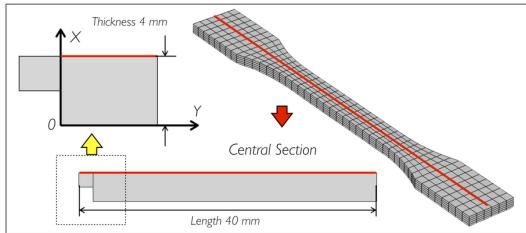


Figure 4. Part geometry

The outlet condition is placed far away from the inlet to avoid disturbance of the flow. If the flow reaches the outlet too early, the Neumann boundary conditions used for the velocity would be incorrect and lead to inaccurate results. Another boundary condition is needed to compute the ϕ values at the beginning of the simulation, by specifying where the ϕ equals 0.5. Respect to the other boundary conditions, this condition is applied between the solution domains of two fluids and it is deactivated once the solution evolves (times greater than zero).

The boundary conditions for the heat transfer specify the temperatures at the mold wall and in domain at the zero time. The temperature at the inlet equals the polymer melt temperature T_{melt} while the air in the cavity equals the mold temperature T_{mold} . These initial values are used as initial conditions for a transient simulation. In addition the heat fluxes across the mold walls are specified

$$-\mathbf{n} \cdot (-k\nabla T) = h \cdot (T - T_{mold}) \quad (20)$$

4. Results

The part chosen as case study to evaluate the crystallization is a dumbbell-shaped tensile specimen with a thickness of 4 mm. Two configurations were analyzed: the small one with a total length of 40 mm and the normal one with a total length of 170 mm. The central section was selected for a 2D simulation, as *Figure 4* reports. The processing parameters were the injection flow rate ($25 \text{ cm}^3/\text{s}$), holding pressure (70 % of the maximum injection pressure), holding time (20 s), cooling time (40 s), melt temperature (220°C) and mold temperature (40°C). We used an

isotactic Polypropylene produced by SABIC AG, Bergen op Zoom, Netherlands with the ID 505 P. This material is characterized by $T_g = -10^\circ\text{C}$ and $T_m = 200^\circ\text{C}$. The viscosity was measured in the range between 210 and 280°C . The pressure-specific volume-temperature (pvT) data provides information about the specific volume changes. It was measured using a SWO Polymertechnik GmbH, Krefeld, Germany pvT-100 device using testing pressures in the range of 100 - 1000 bar, with cooling rates between 1 and 40 K/min. More details are reported in *Spina et al* [9].

The study started with the analysis of the flow front advancement of the melt polymer during filling. *Figure 5* shows the evolution at three different points in time, respectively equal to 0.1 , 0.2 and 0.3 s, using a Cross-WLF model with a constant value of the zero shear viscosity μ_0 and temperature equal to the 220°C . It is possible to note that the resulting polymer-air interface ($\phi = 0.5$) is characterized by a parabolic profile. *Figure 6* reports the distribution at the same points in time using a non-isothermal μ_0 computed with equation (12). The fountain flow effect is pointed-out because the temperature gradient at the wall is high and its effect of viscosity is important. In addition, the position of the air entrapments can be revealed (red dotted circle). The comparison between the isothermal and non-isothermal case is shown in *Figure 7*, in which the two profiles are computed at 0.3 s. The no-slip condition is important for the non-isothermal case because it stops any flow near the wall. This results in an increase of the velocity at the center to maintain a constant flow rate.

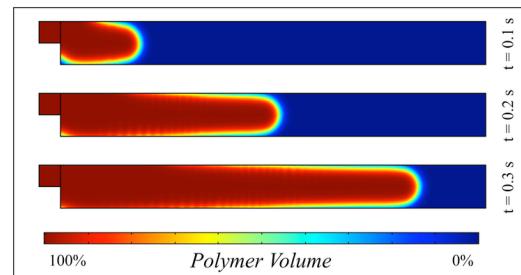


Figure 5. Injection profile with isothermal μ_0

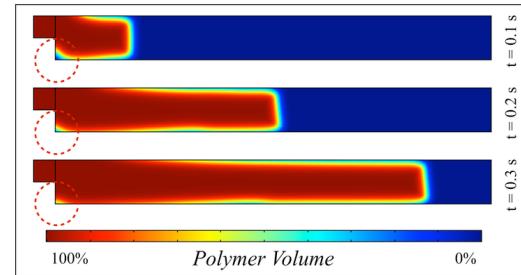


Figure 6. Injection profile with non-isothermal μ_0

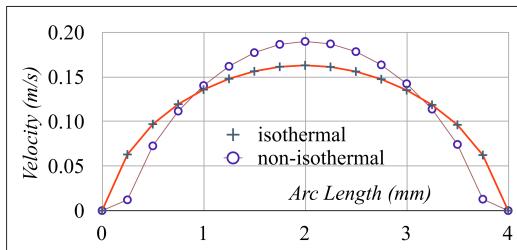


Figure 7. Velocity magnitude comparison

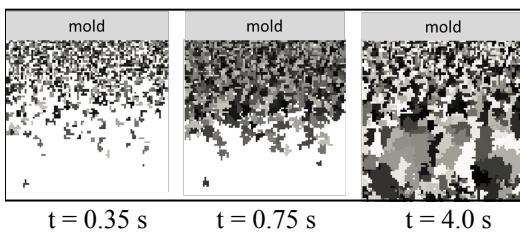


Figure 8. Microstructure formation

Using the results of the COMSOL simulation the crystallization process is simulated using the SphäroSim software package. The temperature, velocity and interface position at 29.8 mm and 30.0 mm distance from the inlet are exported with a resolution of 0.2 mm in thickness direction. This leads to 40 points which describe the 2D simulation area for the simulation of the crystallization process. The high resolution mesh for SphäroSim consists of elements with an edge length of 2.5 μm . Because SphäroSim needs a 3D description of the boundary conditions the 2D boundary conditions of COMSOL are mapped on a 3D mesh with the same shape of the 2D area but a thickness of 2.5 μm . Using these data it is possible to simulate the crystallization process. *Figure 8* shows the simulation of the microstructure formation for a $200 \times 200 \mu\text{m}^2$ simulation area. Point in times from left to right are 0.35 s, 0.75 s and 4.00 s after the injection starts.

7. Conclusions

The crystallization kinetics was successfully simulated. Application to isotactic polypropylene illustrates the complexity of modeling the different material microstructures using COMSOL-SphäroSim integration. Further research must be addressed to link the structural analysis.

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