Development of strain induced crystallisation modelling using the SCORIM process

H. Zuidema, G.W.M. Peters, H.E.H. Meijer
Materials Technology, Eindoven University of Technology
P.O. box 513, 5600 MB Eindhoven, The Netherlands

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Abstract

In contrast to the development of the spherulitical structures during cooling of semi-crystalline polymers, the development of the flow-induced structure is less clear yet. Numerical simulations of start-up experiments have been done, based on the data of a fully characterised polypropylene grade. A comparison is made between results from a shear induced crystallisation model, and results on different functions of the calculated recoverable strain in the melt. It is shown that the shear rate as a starting point for the modelling of flow-induced crystallisation is an not the only one possible, because functions of the recoverable strain in the melt give comparable results. While the latter can be linked to molecular parameters, it should be given preference to.

Keywords: Flow induced crystallisation, functions of recoverable strain, Leonov model, start-up flow.
1 Introduction

In contrast to polymers which turn into a solid amorphous phase during cooling, semi-crystalline polymers can form crystalline regions in an amorphous matrix. Crystallisation of polymers can be strongly influenced by the deformation and thermal history during processing. In particular, this influence is related to the high molecular tail of the molecular mass distribution because of the very slow relaxation behaviour. Consequently, in order to be able to predict the products properties, the morphology of the solidified product has to be predicted accurately. The normal crystallisation process, as for example occurs during cooling of water, is a phase transformation process which is caused by a change in the thermodynamic state of the system. This change can be a lowering of the temperature or an increase in the hydrostatic pressure. Historically, these transformations are described by using a phase diagram assuming the transformation to be in a quasi-equilibrium state. An example of this approach is the description of the growth of the ice layer on the polar see (a Stefan-problem [16]). However, for polymers this approach cannot be used since not one crystallisation temperature is present but a range in temperature where crystallisation occurs. Consequently, the effect on the crystallisation process of supercooling below the melting point can be severe.

Crystallisation of polymers 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 crystallisation process can be subdivided into three phenomena:

Nucleation

Nucleation can be due to overall nucleation from a nucleation agent, pressure induced nucleation, strain induced nucleation and cooling. A nucleus is formed which acts as a starting point for polymer crystallisation. There is no final agreement on the physical background of the nucleation process. For example, Terrill et al. [18] consider, based on experimental evidence (WAXD and SAXD), the nucleation event during spinning of isotactic Polypropylene to be caused by density fluctuations. However, in most cases the nucleation process for a quiescent melt is assumed to be a Poisson point process [11]. For polymers containing nucleation agents also clustered point processes have some importance. In case of flow, nuclei can be created by ordering phenomena in the melt.

Growth

The formed nuclei will grow dependent on the strain history which it experiences; if the nuclei are strained they will grow into threads otherwise they will stay spherical. Threadlike growth is possible by the high molecular tail of the polymer material which has large relaxation times. Due to these high relaxation times these molecules will stay oriented in the maximum principle strain direction. Further growth depends on the shape of the formed nucleus; the spherical nuclei will grow into spherulites while the thread-like nuclei grow mainly perpendicular to the thread. In both situations lamellar growth takes place which results in a shish-kebab structure for the thread-like nuclei while in the spherulites the lamella are present like the spokes in a wheel (figure 1).

Perfection

Perfectioning is the process of improvement of the interior crystalline structure of the crystalline regions. This is also called secondary crystallisation.
In conclusion, dependent on the amount of strain experienced during flow the number and type of the formed nuclei will be different and so will be the crystalline structure. The absence of shear in the center of a injection moulded product results in a spherulitical structure, while in the highly strained regions at the cavity walls a shish-kebab structure is present (figure 2). The local contribution of both types of structures can be combined to give the total degree of crystallinity. In contrast to the development of the spherulitical structure, which can be described quite accurately by using Schneider’s rate equations [15], the development of the flow-induced crystalline structure is not clear yet. In literature, different models are used, some based on strain (Ito [10], Bushman [3]), stress (Verhoyen [19]) or Nakamura-like models (Isajev [9]). However, Bushmans model as well as Nakamura-like models do not provide any information concerning the final structure. In the Ito and Verhoyen work, the number of nuclei depends on the amount of strain/stress. For a process in which, after the mould has been filled, a reverse flow is maintained during solidification/crystallisation of the polymer (SCORIM [2]), this would mean that all nuclei will disappear if the amount of reverse flow equals forward flow!

**Figure 1:** A schematic outline of the concept of crystallisation. The colored dots refer to the colors in figure 2.

**Figure 2:** A cross section of an injection moulded product. The colors refer to the colored dots in figure 1.
However, as is clear from experiments, such a flow history still results in a shear induced layer. The shear rate dependent model of Eder [7], a phenomenological one, has the advantage that it predicts the structure properties such as the number of shish-kebabs, their length, etc. On the one hand, this model shows a good description of the phenomena as observed during experiments [12]. On the other hand, this model is based on dynamics of the flow, not on the dynamics of the molecules in the melt. This leads to the proposition that another type of modelling should be used, for instance, the number of nuclei dependent on functions of the recoverable strain, which is considered to be a representative measure for the molecular strain.
2 Modelling

Balance equations

In order to be able to predict the flow-induced strain and orientation during flow in the cavity, equations for the evolution of the recoverable strain are incorporated in VIp (Polymer Processing & Product Properties Prediction Program), a program for the numerical simulation of all stages of the injection moulding and transfer moulding process (Douven [6], Caspers [4], Zoetelief [20], Haagh [8]). These equations will be solved decoupled, after solving the balance equations:

\[
\dot{\rho} + \rho \nabla \cdot \vec{v} = 0
\]
\[(1)\]

\[
\nabla \cdot \vec{\sigma} + \rho \ddot{f} = \rho \ddot{v}
\]
\[(2)\]

\[
\vec{\sigma} = \vec{\sigma}^e
\]
\[(3)\]

\[
\rho \dot{\varepsilon} = \sigma : \mathbf{D} - \nabla \cdot \vec{h} + \rho r_h
\]
\[(4)\]

in which \( \rho \) is the density, \( \vec{v} \) is the velocity vector, \( \vec{\sigma} \) is the Cauchy stress tensor, \( \ddot{f} \) is the specific (i.e. per unit mass) body force, \( \mathbf{D} \) is the rate of deformation tensor, \( \varepsilon \) is the specific internal energy, \( \vec{h} \) is the heat flux vector and \( r_h \) is the specific heat source. The balance equations are completed with constitutive equations.

Recoverable strain and orientation

The recoverable strain present in the melt during processing depends on the mechanical and thermal history of the material. It is pointed out by Baaijens [1] that the compressible Leonov model gives a reasonable good description of the material behaviour and the flow induced orientation during the injection moulding process. Figure 3 shows a schematic representation of the deformation. In the loaded state the material is deformed elastically and plasticly (\( C_t \)), while after removal of the load, only the plastic deformation remains (\( C_p \)). Consequently, in the compressible Leonov model the deformation gradient tensor \( \mathbf{F} \) is split in an elastic part \( \mathbf{F}_e \) and a plastic part \( \mathbf{F}_p \) (figure 4)

\[
\mathbf{F} = \left( \nabla_0 \dot{\varepsilon} \right)^e = \mathbf{F}_e \mathbf{F}_p
\]
\[(5)\]
in which \( \vec{x} \) is the position vector.

For the material time derivative of the elastic Finger tensor \( \mathbf{B}_e = \mathbf{F}_e \mathbf{F}_e^T \) this results in

\[
\dot{\mathbf{B}}_e = \left( \mathbf{L}_e - \frac{1}{3} tr (\mathbf{D}) \mathbf{I} \right) \mathbf{B}_e + \mathbf{B}_e \left( \mathbf{L}_e - \frac{1}{3} tr (\mathbf{D}) \mathbf{I} \right)
\]  
(6)

in which \( \mathbf{L}_e \) is the elastic part of the velocity gradient tensor, \( \mathbf{D}_p \) the plastic part of the rate of deformation tensor and \( \mathbf{I} \) the unit tensor. For \( \mathbf{D}_p \) Leonov proposed the following constitutive expression:

\[
\mathbf{D}_p = \frac{1}{4\theta} \left( \mathbf{B}_e - \mathbf{B}_e^d \right)
\]  
(7)

This results in

\[
\mathbf{B}_e = \mathbf{L}^d \mathbf{B}_e + \mathbf{B}_e \mathbf{L}^{dc} - \frac{1}{2\theta} \left( \mathbf{B}_e \mathbf{B}_e - \mathbf{I} - \frac{1}{3} \left( tr (\mathbf{B}_e) - tr (\mathbf{B}_e^{-1}) \right) \right) \mathbf{B}_e
\]  
(8)

Notice that by choosing the appropriate expression for \( \mathbf{D}_p \) most of the known viscoelastic models can be regained or new viscoelastic models can be obtained (Peters [13]). Elastic stresses are decomposed in a hydrostatic part and the extra stress tensor \( \mathbf{\tau}_e \) (the deviatoric part)

\[
\mathbf{\sigma}_e = p\mathbf{I} + \mathbf{\tau}_e
\]  
(9)

For the multi-mode case, the extra stress tensor is written as

\[
\mathbf{\tau}_e = \sum_{j=1}^{n} \frac{\eta_j}{\theta_j} \mathbf{B}_{e_j}^d
\]  
(10)

in which \( \eta_j \) the Leonov viscosity for the j-th mode, \( \theta_j \) the Leonov relaxation time for the j-th mode and with n different \( \mathbf{B}_{e_j}^d \). With every \( \mathbf{B}_{e_j}^d \) different plastic rate of deformation tensors \( \mathbf{D}_p \) can be defined!

**Thermorheological simple materials**

For many polymers it is commonly found that, for a set of isothermal curves (creep, relaxation, modulus, viscosity, etc.) measured at different temperatures, the curves can be shifted along the logarithmic
time axis, resulting in one master curve. The shift depends on the temperature difference between the master curve and the curve that has to be shifted. This behaviour implies that

$$\theta_j = a_T(T)\theta_{j0}$$  \hspace{1cm} (11)

in which $a_T(T)$ is the time-temperature shift function and $\theta_{j0}$ is the relaxation time for the $j$-th component at the reference temperature for the master curve. The shift function $a_T(T)$ can be described using the WLF-equation if $T \geq T_g$

$$\log(a_T(T)) = \frac{C_1(T - T_0)}{C_2 + T - T_0}$$  \hspace{1cm} (12)

while below $T_g$

$$a_T(T) = a_T(T_g)$$  \hspace{1cm} (13)

Modelling aspects

Because in most practical applications the thickness of an injection moulded product is small compared to the other dimensions, the cavity can be described by using a Hele-Shaw or thin film approximation. The main assumptions made are:

- the inertial and body forces are negligible compared to the viscous forces,
- the pressure is constant across the thickness,
- the velocity component in the thickness-direction is small compared to those tangent to the midplane,
- the velocity gradients parallel to the midplane are small compared to those in the thickness-direction,
- thermal conductivity parallel to the midplane is negligible compared to the conduction in the thickness direction.

Consequently, the pressure only has to be calculated in the midplane of the cavity (2D), while the velocity and temperature have to be calculated fully 3D, resulting in a 2.5D (two-and-a-half-D) modelling. For calculating the flow induced recoverable strain- and orientation, a decoupled modelling is used, i.e. a 2.5D, non-isothermal generalised Newtonian flow modelling (Caspers [4]) giving the kinematics which are used in the fully 3D viscoelastic calculation. This is solved using a 4th order Runge-Kutta explicit integration scheme. These calculations can easily be extended to fully 3D (Haagh [8]).
3 Experiments

While standard experiments are not suited to create extreme situations concerning flow-induced crystallisation comparable with the situation during injection moulding of semi-crystalline polymers, the SCORIM process (Shear Controlled Orientation Injection Moulding) will be used to create these extremes, acting as a test case for the modelling of crystallisation kinetics during injection moulding. Moreover, because the processing conditions can be controlled, processing along selected routes can be used as a starting point for numerical simulations. During this process a flow is maintained in the mould after it has been filled, during solidification/crystallisation of the polymer. As crystallisation is enhanced by the deformation of the melt, the flow will increase the degree of crystallinity, a layered structure over the thickness of the cavity is the result (figure 5). Analysing the flow and crystallisation kinetics in this process will lead to a more detailed understanding of the flow-induced crystallisation kinetics.

Figure 5: The resulting layered structure over half the thickness of the sample after the SCORIM process.

The experiments done by Jerschow [12] resemble one cycle of the SCORIM process. In these, a duct (155 x 10 x 1 [mm$^3$]) is filled with polymer at a high temperature (200°C). After filling the flow is stopped and a period of 20 minutes is prolonged to get rid of filling history. Afterwards the duct is quenched to the desired experimental temperature (150°C). Next the flow in the duct is started again for a chosen time. In this way experiments can be done for different shearing times and shear rates. After this shearing procedure, which lasts up to 30 seconds, the light intensities at perpendicular and parallel polars are monitored for a time period of 30 to 90 minutes. Finally, the duct is cooled down to room temperature. More detailed information can be found in [12]. For experiments using different shearing times and shear rates, the thickness of the flow-induced layers can be obtained by making microtome cuts parallel to the flow direction. Three different layers are present if the shear flow is strong enough (figure 2): a highly oriented layer near the walls of the duct, a core with large spherulites and a fine grained layer in between. Measuring the thickness of both layers resulted in a relation between the used shearing time and accompanying calculated shear rate at the boundaries of these layers (figure 6). From the experiments done by Jerschow [12] it is concluded that for shear induced crystallisation precursors are formed during the flow, which reach the same effectiveness at $\dot{\gamma}^A t^2 = constant$. In the same way it is concluded that the boundary between the fined grained layer and the core is characterised by $\dot{\gamma}^D t^2 = constant$. Finally, from these measurements a shear-induced crystallisation model was extracted by Eder [7].
Figure 6: Measured distance from the wall of the boundaries of the shear induced layers (top) and accompanying shear rate at that position (bottom), for a wall shear rate of approximately $115 \ [s^{-1}]$ (reproduced from [12]).
4 Material characterisation

For the numerical simulation of the experiments described in the previous section, the properties of the polymer have to be known. The material was polypropylene KS10 (Borealis). As, for this material, a pVT model is not available at this moment, the specific volume is set constant at:

\[
\begin{align*}
V_m &= 0.0009225 \text{ m}^3 \text{ kg}^{-1} \\
\end{align*}
\]

However, it is expected that this only causes a small delay in the development of the recoverable strain, having hardly any influence on the results. The viscosity \( \eta \) is modelled using a Carreau model in which \( \dot{\gamma} \) is the shear rate, using the variables in table 1:

\[
\eta = \frac{\eta_0}{(1+(\dot{\gamma}/\lambda)^m)^{1/n}}
\]

Table 1: Parameters for the Carreau model for the viscosity of the polypropylene KS10 (Borealis).

This viscosity is not crystallinity dependent as the experiments done are isothermal at a temperature which hardly enables lamellar crystal growth. The thermal capacity \( c_p \) is set constant at \( c_p = 2136.9 [J kg^{-1} K^{-1}] \) and the thermal conductivity at \( \lambda = 0.21 [W m^{-1} K^{-1}] \).

The rheological behaviour for the computation of the flow induced recoverable strain and orientation is described by the compressible Leonov model. The parameters are determined using oscillatory shear experiments, shifted to the reference temperature \( T_{Lr} = 200^\circ C \). The fits for the storage and loss modulus are shown in figure 7, while the parameters are listed in table 2. The shift factor \( log a_T \) as determined by Jerschow [12] equals 0.0106 [K^{-1}].

![Figure 7: Experimental (symbols) and fitted (lines) storage and loss modulus for the iPP (KS10, Borealis).](image-url)
Table 2: Linear viscoelastic parameters for the compressible Leonov model of the polypropylene KS10 (Borealis).

<table>
<thead>
<tr>
<th>$j$</th>
<th>$\theta_j [s]$</th>
<th>$G_j [Pa]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>29.7434</td>
<td>$0.0033 \times 10^4$</td>
</tr>
<tr>
<td>2</td>
<td>1.5679</td>
<td>$0.1208 \times 10^4$</td>
</tr>
<tr>
<td>3</td>
<td>0.1144</td>
<td>$1.2099 \times 10^4$</td>
</tr>
<tr>
<td>4</td>
<td>0.0080</td>
<td>$5.4568 \times 10^4$</td>
</tr>
</tbody>
</table>
5 Results

Although the crystallisation model of Eder is based on the shear rate, also a comparison can be made between the thickness of the described layers and the (invariants of the) flow induced recoverable strain calculated using the Leonov model. Simulations have been done for experiments with a wall shear rate of approximately 79 and 115 \([\text{s}^{-1}]\). The experimentally determined distance from the wall of the boundaries of the flow induced and fine grained layers are reproduced in figure 8 for all experiments. Because it is not feasible at this moment to do numerical simulations including the monitoring period for the light intensity measurements (up to 90 minutes), simulations are done until the values for the recoverable strain are decreased to approximately 0.5 % of the maximum values (100 seconds at maximum for the first mode). As all the recoverable strain present in the melt has decreased to zero far before the complete monitoring time of 90 minutes, it does not make sense to relate this strain to the thickness of both layers described. Consequently, it is postulated that the influence of the recoverable strain on the crystallisation process should be something like a time integral of (a function of) the actual recoverable strain. Moreover, the difference between sherulitical crystallisation and shish-kebab crystallisation is caused by the orientation of the high molecular tail of the molecular mass distribution. The (amount of) orientation is described by the difference of the main eigenvalues of the elastic Finger tensor, which is called the first normal recoverable strain difference \(N^B_1\). Simulations are done for experiments with different shearing times, including the relaxation period of the recoverable strain. Results for the time integral of the first normal recoverable strain difference as a function of shearing time and position in the cavity are presented in figure 9 and compared with the position of the layer boundaries. From the contours the values of this integral at the experimentally determined layer boundaries can easily be obtained (figure 10). In the same way simulation results are obtained for the time integral of the squared first normal recoverable strain difference (figures 11, 12). The most striking feature in figures 10 and 12 is that for both experiments with different wall shear rates, the results do match for all modes. All results for \(\int_0^T N^B_1 \, dt\) (figure 10) even show the same dependence on the shearing time although the values are smaller for modes with smaller relaxation times. For the \(\int_0^T N^B_1^2 \, dt\) however (figure 12), the values are almost constant for the mode with the largest relaxation times.

Figure 8: Experimentally determined distance from the wall of the boundaries of the flow induced (\(*\)) and fine grained layers (\(\circ\)) for experiment with a wall shear rate of approximately 79 (left) and 115 \([\text{s}^{-1}]\) (right) (reproduced from \([12]\)).
Figure 9: Numerically determined contours for the time integral of the first normal recoverable strain difference for experiments with a wall shear rate of approximately 79 (left) and 115 [s$^{-1}$] (right). Results are for mode 1 (top), 2 (middle) and 3 (bottom). The centre of the cavity is located at position zero.
Figure 10: Numerically obtained values for the time integral of the first normal recoverable strain difference at the position of the boundaries of the flow induced (●) and fine grained layer (○) for experiments with a wall shear rate of approximately 79 [s\(^{-1}\)] (red) and 115 [s\(^{-1}\)] (blue) Results are for mode 1 (top), 2 (middle) and 3 (bottom).
Figure 11: Numerically determined contours for the time integral of the squared first normal recoverable strain difference for experiments with a wall shear rate of approximately 79 (left) and 115 [s$^{-1}$] (right). Results are for mode 1 (top), 2 (middle) and 3 (bottom). The centre of the cavity is located at position zero.
Figure 12: Numerically obtained values for the time integral of the squared first normal recoverable strain difference at the position of the boundaries of the flow induced (×) and fine grained layer (○) for experiments with a wall shear rate of approximately 79 (red) and 115 [s⁻¹] (blue) Results are for mode 1 (top), 2 (middle) and 3 (bottom).
6 Discussion

From the experiments done by Jerschow [12] and the resulting shear induced crystallisation model of Eder [7], it is concluded that for shear induced crystallisation precursors are formed during the flow, which reach the same effectiveness at $\dot{\gamma}^4 t_s = \text{constant}$. In the same way it is concluded that the boundary between the fined grained layer and the core is characterised by $\dot{\gamma}^2 t_s = \text{constant}$. This means that the derivative of the number of precursors $N$ scales with the first normal recoverable strain difference $N_1^p$ and also the derivative of the length of the formed shish scales with the first normal recoverable strain difference $N_0^p$. Combining this means that the number of precursors $N$ is related to $\int_0^t N_1^p \, dt$ and the total length of the shish to $\int_0^t N_0^p \, dt$, as is shown in figures 10 and 12. In this case, it is assumed that from the start of the experiment the flow field in the strip is fully developed, resulting in a constant velocity profile over the thickness of the strip for the entire length. This is the reason for the constant specific volume in the material parameters. Moreover, it is to be expected that the only difference in case of a specific volume dependent on pressure and temperature (like Chiang [5]) is a very small delay in the development of the recoverable strain, having hardly any influence on the results.

Although the evolution of the recoverable strain is described using the Leonov model, also different models like the Giesekus model, the Phan-Thien Tanner model or the recently proposed FETA models (Peters [14]) can easily be implemented. In conclusion, these results are promising for the development of a flow induced crystallisation model, which is based on the recoverable strain; a measure for the deformed state of the molecules. However, more simulations on different experiments (Swartjes [17]) have to be done to confirm this.
7 Conclusions

From these results it is clear that the choice for the critical shear rate as a function of shearing time for the description of flow induced crystallisation is not the only one. Using the time integral of the squared first normal recoverable strain difference gives comparable results. Moreover, the shear rate is included in the development of the first normal recoverable strain difference, while the time integral represents the shearing time. While the first normal recoverable strain difference is related to the molecular state of the melt, it should be given preference to.
References


[17] Swartjes et. al. In-situ X-ray measurements of the influence of pure elongational flow on the crystallisation kinetics *Personel communications*

