Polymer Injection Molding: Flow-induced Crystallization

A model for the description of the combined process of quiescent and flow-induced crystallization of polymers is presented. With such a model it should become possible to predict in detail the spatial distribution of the crystalline structure in a product and, from that, the final mechanical properties, shape and dimension stability of the product. However, the latter is not discussed here. The model is based on the work of Schneider et al. (1998) and Eder et al. (1990), where the shear rate was taken as the relevant parameter. A viscoelastic model is added from which the resulting recoverable strain (expressed by the elastic finger tensor or the related viscoelastic stress) with the highest relaxation time is used as the driving force (instead of the shear rate) for flow-induced crystallization (Zuidema 2000). Some illustrative results are shown for a polypropylene. The comparison with experimental results from literature shows good agreement.

1. Introduction

The present model for flow-induced crystallization is based on a combination of experiments from literature and a full description of the thermomechanical history of these experiments.

Crystallization of polymers is kinetically controlled and the motion involved refers to the transport of molecules from the disordered liquid phase to the ordered solid phase. The crystallization process can be subdivided into three stages: (i) nucleation, which can have different causes such as overall nucleation from a nucleation agent, pressure-induced nucleation, strain-induced nucleation and cooling. Nuclei are formed, which act as starting points for polymer crystallization. There is no complete agreement on the underlying physics, the nucleation process for a quiescent melt can be described by a Poisson point process. In the case of flow, nuclei can be created by flow-induced ordering phenomena in the melt. (ii) The nuclei formed will grow, depending on the thermomechanical history they experience; if the nuclei are sufficiently strained they will grow into threads, otherwise they stay spherical and will grow further radially. The thread-like nuclei mainly grow perpendicular to the thread. In both cases lamellar growth takes place, which results in a shish-kebab structure for the thread-like nuclei. In the spherulites the lamella are present like spokes in a wheel. (iii) Perfecting is the process of improvement of the interior crystalline structure of the crystalline regions. This is also referred to as secondary crystallization.

Crystallization of polymers is influenced by the thermomechanical history during processing. Dependent on the amount of strain experienced during flow, the number and type of formed nuclei will be different, as will be the final crystalline structure. For example, the absence of shear in the center of an injection-molded product results in a spherulitical structure, while in the highly strained regions near the cavity walls a shish-kebab structure can be present (Fig. 1). It is this internal structure that determines the final product properties.

2. Modeling

Based on the results from Vleeshouwers and Meijer (1996), who detected a pronounced influence of molar mass on shear induced crystallization, it is postulated that thread-like growth is governed by the high-end tail of the molecular mass distribution, which is characterized by its largest relaxation times. This results in two sets of differential equations for quiescent and flow-induced crystallization, respectively, which are combined with a model for the viscoelastic stresses. Here a multi-mode Leonov model is applied. The advantage of this model is that a reasonable description for shear flows is obtained using linear viscoelastic data only. The applicability is then restricted to shear-dominated processes such as injection molding. Instead of viscoelastic stress we have chosen to formulate this model in terms of the volume invariant recoverable elastic strain tensor $B_1$ representing the orientation of the molecules:

$$B_1 + \frac{1}{20}(B_1 B_1 - I - \frac{1}{2}(tr(B_1))B_1) = 0 \quad (1)$$

For quiescent crystallization, leading to spherulitical structures, the set of equations reads (Schneider et al. 1998):

$$\phi_3 = 8\pi x \quad (\phi_3 = 8\pi N)$$
$$\phi_2 = G\phi_3 \quad (\phi_2 = 8\pi B_{11})$$
$$\phi_1 = G\phi_2 \quad (\phi_1 = S_{11})$$
$$\phi_0 = G\phi \quad (\phi_0 = V_{tot}) \quad (2)$$

in which $x$ is the nucleation rate and $G$ is the crystal growth rate. This set of equations fully characterizes the spherulitical structure, i.e., the mean specific
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For flow-induced crystallization the set of differential equations reads (Zuidema 2000, Zuidema et al. 2001):

\[
\psi_3 + \frac{\psi_3}{\tau_s} = 8\pi J_3 g_{\phi_s} \quad (\psi_3 = 8\pi N_f) \\
\psi_2 + \frac{\psi_2}{\eta} = \psi_2 J_2 g_{\phi_s} \quad (\psi_2 = 4\pi L_{f,100}) \\
\psi_1 = G\psi_s \quad (\psi_1 = S_{f,100}) \\
\psi_0 = G\psi_t \quad (\psi_0 = V_{f,100})
\]

in which \( J_2 \) is the second invariant of the deviatoric part of the recoverable strain (\( S_J \)-model):

\[
J_2(B^s) = \frac{1}{2} B^s : B^s
\]

is the driving force for flow-induced nucleation and growth. From the eigenvectors of the recoverable strain tensor \( B \), the local orientation is determined. This set of equations gives a full description of the flow-induced oriented, crystalline structure; i.e., the specific number of flow-induced nuclei \( N_f \), and the total length \( L_{f,100} \), surface \( S_{f,100} \) and volume \( V_{f,100} \). The unknown parameters are the relaxation time \( \tau_s \) for the nuclei, the relaxation time \( \tau_t \) for the shish kebab, and scaling factors \( g_{\phi} \) and \( g_{\phi} \).

In the case of the Eder model, the driving force for flow-induced crystallization is the shear rate \( \gamma \) and \( J_2 \) should be replaced by \( \gamma^2 \) in Eqn. (3) and the values of the parameters \( g_{\phi} \) and \( g_{\phi} \) should be adapted.

Both crystallization models can be combined with a model for impingement as, for example, the Avrami model in which \( \xi_n \) represents the degree of space filling.

\[
-\ln(1 - \xi_n) = \phi_s + \psi_0
\]

The overall degree of crystallinity \( \xi \) is obtained by multiplying the degree of space filling \( \xi \) with the degree of crystallinity in each spherulite/shish kebab.

As nucleation sites are considered to act as physical cross-links, the maximum rheological relaxation time \( \theta_r \) is coupled with the number of nucleation sites. A simple linear relationship is chosen:

\[
\theta_r = a_\phi(T)\theta_{\phi_r} \left( 1 + \frac{\alpha N_f}{g_{\phi}} \right)
\]

in which \( \theta_{\phi_r} \) is the rheological relaxation time at the reference temperature, \( a_\phi(T) \) the time-temperature shift function and \( \alpha \) the scaling parameter of the influence of the number of nuclei on the rheological relaxation time. The interplay between rheology and flow-induced crystallization can therefore be rather complex. The model is implemented in VIP, a FEM

number of spherulites \( N \), their radius \( R_{tot} \), surface \( S_{tot} \) and volume \( V_{tot} \).

Figure 1
Injection-molded product (cross-section) of polypropylene.
3. Results

Owing to their larger relaxation times, high molecular weight molecules will facilitate nucleation/crystallization and, therefore, it is postulated that the flow-induced structures will correlate most strongly with the viscoelastic mode with the highest relaxation time. Or, more formally, the number of flow-induced nuclei and/or the growth rate of the flow-induced structures is a functional of the invariants of the elastic finger tensor corresponding to the highest relaxation time. If this statement is true, then material that experienced a history leading to the same value of this (unknown) functional should show the same flow-induced structure, and thus the same optical properties.

Short-term shear experiments (duct flow) were performed by Jerschow (1994) with a wall shear rates of 79 and 115 s$^{-1}$ and different shear times (material: iPP K2Xmod, Borealis). The distance from the wall of the boundaries of flow-induced oriented and fine-grained layers were determined optically. These clearly visible transitions are used to verify our hypothesis.

The following is restricted to the second invariant of the deviatoric part of the volume invariant elastic finger tensor. It is interesting to see the equivalence of this tensor, and its second invariant, with the tensor order parameter as defined in the Onsager theory (Larson 1999) for the transition from isotropic to nematic of nondilute solutions of rod-like molecules. This order parameter is defined as the deviatoric

![Figure 2](image)

*Figure 2*  
Calculated values for the time integral of the second invariant of the recoverable strain at the position of the layer transitions. Oriented/fine grained (*), grained/normal (○) for experiments with a wall shear rate of 79 and 115 s$^{-1}$. Results are for mode 1 (a), 2 (b), and 3 (c).
Figure 3
Visualization of the calculated structure development ($t = 1.2s$ after quenching) together with the local (solid) and global (line) degree of crystallinity. Black indicates the amount of interface between spherulites and shish kebabs. The center of the duct is at 0 m, the surface at $5 \times 10^{-1} m$.

part of the orientation configuration tensor $S = \langle \hat{u}\hat{u} \rangle$. The maximum of the scalar order parameter $S$ is defined by $S^2 = \frac{1}{2} S: S$ (Larson 1999). The most simple functional, the integral in time, of $J_2(B^2)$ is chosen to be correlated with the structure.

For both flow rates and each shear time the value of this integral was calculated at the experimentally determined transition positions. This was done for a three-mode model (i.e., three relaxation times obtained from rheological data, $G'$ and $G''$). The parameters in the model are obtained by fitting only one benchmark experiment (wall shear rate $72s^{-1}$, shear time 7s).

The striking observation is that the values for this time integral are almost constant for the mode with the largest relaxation time (Fig. 2), while they vary strongly for the other two modes. This supports the basic concept stated above that the flow-induced structure will correlate most strongly with the viscoelastic mode with the highest relaxation time and, therefore, this is a good candidate for the driving force in a model for flow-induced crystallization.

For steady-state experiments (Eder et al. 1990), simulations were carried out giving the development of stresses until a steady state was reached in the duct, including a spatially steady time integral of the second invariant of the recoverable strain tensor. Numerically, quenching was imposed by forcing the wall temperature to be $T_w = 293 K$. With the rate equations, a complete description of the final structure is available, which can be used for visualizing the development of the resulting structure during subsequent quenching of the steady state. Results are shown for a position close to the entrance of the duct.
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Figure 4
Visualization of the calculated structure development ($t = 2.2\text{s}$ after quenching) together with the local (solid) and global (line) degree of crystallinity. Black indicates the amount of interface between spherulites and shish kebabs. The center of the duct is at $0\text{ m}$, the surface at $5 \times 10^{-1}\text{m}$.

(Figs. 3 and 4). The spherulitical and oriented (shish kebab) structures are shown together with the local degree of crystallinity. The slow cooling in the center of the duct enables few crystals to grow at low rates, resulting in a more coarse crystal structure compared to regions closer to the wall of the duct. There, the faster cooling enables formation of nuclei at lower temperatures. Consequently, more nuclei are formed that grow at higher rates, resulting in a fine-grained structure next to the highly oriented layer at the wall.

4. Discussion
A model is presented that allows for the prediction of the crystalline structure distribution in injection-molded products that have experienced a complex thermomechanical history. This structure is the input for the determination of the final product properties. For example, with the detailed description of the crystalline structure and knowing the PVT behavior, the density distribution in a product can be computed and from that, residual stresses, resulting finally in the prediction of dimensional stability for semi-crystalline polymers (as comparable to those for amorphous polymers, see Polymer Injection Molding: Modeling for Properties). The model is validated by comparing numerical with experimental results from the literature and the agreement is good.

See also: Polymer Injection Molding: Moldflow; Polymer Injection Molding: C-Mold; Polymer Injection Molding: Multimaterial Molding; Polymer
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Bibliography


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