Model Development and Validation of Crystallization Behavior in Injection Molding Prototype Flows

Frederico J. M. F. Custódio, Rudi J. A. Steenbakkers, Patrick D. Anderson, Gerrit W. M. Peters,* Han E. H. Meijer

To control the final properties of semi-crystalline polymer products, an accurate prediction of the material microstructure developed upon processing is required. For that purpose a model for flow-enhanced nucleation of semi-crystalline polymers is proposed, which relates molecular deformation with the enhancement of crystallization. Flow kinematics, computed in a decoupled fashion, are used to solve a coupled viscoelastic stress — crystallization problem. Morphological features concerning the number, size, and shape of crystalline structures are predicted and a comparison is made with experimental results reported by Housmans et al.[1,2] in which the morphology development of an isotactic polypropylene (iPP) resin was studied.

Introduction

The microstructure of semi-crystalline polymers results from a variety of physical changes that occur during processing. Notably, in injection molding such changes take place under extreme conditions characterized by high shear rates, high pressure levels, high cooling rates, and steep temperature gradients. The morphology of the material develops according to these conditions and the part geometry. An important physical phenomenon during processing is crystallization, which is coupled to the flow history: flow accelerates crystallization, while crystallization changes the rheological behavior, and thus the flow. Furthermore, crystallization plays a dominant role in the final properties of injection molded parts. However, the effect of crystallization on macroscopic properties is difficult to predict and, therefore, also difficult to control. Typically the microstructure of an injection molded part, when visualized under polarized optical light microscopy, consists of different layers: a highly oriented layer close to the surface, a transition layer, a second oriented shear layer, a fine-grained layer, and a spherulitical core.[3] This layer-type morphology introduces a high degree of anisotropy in physical properties.[4,5] The effect of processing conditions on the morphology of the microstructure of injection molded parts has been extensively investigated. For example, Viana et al.[6] found the oriented layer/core ratio to vary most strongly with varying injection speed and injection temperature.

In order to unravel the intrinsic relation between product properties and the underlying crystalline morphology, research effort has been devoted to predict the microstructure of injection molded parts of semi-crystalline materials. Most of the studies focused on isotactic polypropylene (iPP), due to its high potential for property
tuning and its vast use in applications, where crystallinity determines the mechanical and optical properties.

Pantani et al.\cite{Pantani2009} gave an extensive review on available models and experimental techniques to predict and characterize the morphology of injection molded parts. The authors proposed a model to predict the morphology of injection molded iPP, in which flow kinematics are computed using a lubrication approximation. Polymorphism was accounted for, using the Avrami–Evans–Nakamura equation to describe the crystallization kinetics of the mesomorphic phase, while the evolution of the $\alpha$ phase was modeled using Kolmogorov–Avrami model.\cite{Avrami1940, Evans1956, Nakamura1978} The growth rate of spherulites was described by the Hoffman–Lauritzen expression.\cite{Hoffman1956, Lauritzen1971} Smirnova et al.\cite{Smirnova2003} used a differential set of Avrami equations to predict crystallinity and the average size of spherulites in injection molding, but in their study only temperature effects were taken into account.

In a different study, Pantani et al.\cite{Pantani2010} investigated the effect of varying the packing pressure on the morphology of injection molded samples. The effect of pressure on crystallization kinetics was also assessed in a study by Watanabe et al.\cite{Watanabe2007} in which the authors measured the half time, $t_{1/2}$, for crystallization (defined as the time at which the volume fraction of crystallized material reaches 50%) and verified that pressure indeed simply acts as to increase undercooling.

Van der Beek\cite{Van2009, Beek2011} experimentally studied the combined effect of pressure, cooling rate, and shear deformation on the specific volume of iPP, in a new PVT (pressure-volume-temperature) apparatus which allows PVT measurements at high cooling rates ($100^\circ$C·s$^{-1}$) and pressures (up to 100 MPa). Additionally, the device makes it possible to generate flows prior to or during cooling with shear rates in the order of $10^2$–$10^3$ s$^{-1}$. Experiments like these will certainly provide the input for further improvement and validation of theoretical models.

Flow effects on crystallization in injection molding simulations are often taken into account by adopting a
modified version of the Nakamura equation.\[^{[17]}\] Within this approach, Hieber\[^{[18]}\] defined a characteristic time for crystallization that was made dependent on temperature, pressure, and the absolute value of the shear stress. In an early work Patel et al.,\[^{[19]}\] modeling melt spinning, used a viscous model for the stress in which the viscosity was crystallinity dependent and in the applied Nakamura equation the crystallization rate pre-factor was made stress dependent, thus creating a full coupling between the flow behavior and the crystallization.

Isayev et al.,\[^{[20,21]}\] combined the Nakamura equation with an early version of a shear-induced crystallization model by Janeschitz-Kriegel and coworkers.\[^{[22,23]}\] The influence of crystallinity on the viscosity (a viscous model was used) was assumed to be negligible. Parameters for the shear-induced crystallization model were obtained from separate extrusion experiments. The shear-induced skin layer distribution in an injection molded strip was predicted for varying injection speed and compared with experiments. The model was extended to predict spherulite size distributions.\[^{[24]}\] A similar approach was chosen by Guo et al.,\[^{[25]}\] and applied to three different commercial iPPs, studying the influence of the average molecular weight. Isayev et al.,\[^{[26]}\] studied in a similar way iPPs polymerized using metallocene and Ziegler–Natta catalysts.

Kim et al.,\[^{[27]}\] modified the crystallization rate constant in the Nakamura model, making it dependent on the shear rate. They tried to predict the thickness of the oriented shear-induced layer using a thermodynamic approach, in which viscoelastic stresses were computed to find changes in entropy associated with the flow. Making use of Flory’s expression\[^{[28]}\] that relates the equilibrium melting temperature, \(T_m\), with changes in entropy, the authors could determine the increase in the nominal melting temperature resulting from the entropy decrease imposed by the flow. A similar approach was followed by Titomanlio and Lamberti\[^{[29]}\] for the simulation of film casting. In ref.,\[^{[25]}\] the transition from spherulitical core to oriented shear layer was assumed to take place when the local temperature would equal the calculated \(T_m\). Even though their results qualitatively describe the experimental data, they still fall short from providing morphological detail.

Summarizing, most of the numerical studies on injection molding of semi-crystalline materials give little insight in the morphology developed, failing to provide information about the shape and dimensions of oriented crystalline structures. Also, the crystallization models employed lack molecular understanding, and they do not couple flow-induced crystallization with melt rheology. Furthermore, often similar growth mechanisms for non-oriented and oriented crystals are assumed, which is in clear contradiction with experimental evidence that shows the growth kinetics of a spherulite to be profoundly different from that of a shish.\[^{[30]}\]

Advances in the physical understanding of flow-associated effects on crystallization have recently been reviewed by Somani et al.,\[^{[31]}\] and Kumaraswamy.\[^{[32]}\] It has been experimentally observed that long chains, the high end tail of the molecular weight distribution, play a dominant and decisive role accelerating the kinetics of flow-induced crystallization.\[^{[33–36]}\] Seki et al.,\[^{[35]}\] showed that with the addition of just 1 wt.-% of chains with a weight-averaged molecular weight \(M_w\) five times larger than that of the matrix resin, crystallization kinetics are profoundly changed. Special experimental setups have been developed to perform short-term shear experiments in semi-crystalline polymer melts at strain rates close to real processing conditions.\[^{[29,34,37–39]}\] In these experiments a polymer melt is held above its equilibrium melting temperature for some time, such that any residual ordering or structure is erased, and subsequently cooled to a desired crystallization temperature at which the material is subjected to a brief shear deformation. The crystallization temperature is chosen such that quiescent crystallization takes place on a time scale much larger than the flow times investigated. The changes in microstructure are monitored during and after the flow. These studies provide insight into the kinetics of flow-enhanced nucleation and its dependence on flow conditions, as well as morphological detail of oriented crystals. Mechanical deformation of the melt (shear or extension) was found to significantly enhance nucleation, and the increase in deformation rate to be more effective than that of deformation time. In their early work on dilute solutions in elongational flows, Keller and Kolnai\[^{[40]}\] already identified an abrupt change in birefringence upon reaching a critical strain rate, which was associated by the authors to a coil–stretch transition of the chain conformation. They reasoned that this phenomenon could also occur in entangled polymer melts beyond a critical strain rate, and lead to the formation of oriented crystals (row nucleation). More recently, Seki et al.,\[^{[35]}\] used short-term pressure-driven shear experiments on iPP melts at constant wall shear stress and identified a critical shear stress, needed to induce the transition from spherulitical to oriented crystal growth, which was found to decrease with the addition of long chains. Comparing turbidity, birefringence, optical microscopy, and transmission electron microscopy data for these experiments; they concluded that this stress threshold has to be surpassed to generate threadlike precursors that template row-nucleated structures (shish).

In an attempt to unify all these findings, Van Meerveld et al.,\[^{[41]}\] classified different flow regimes according to what they called the Deborah number, defined as the product of the strain rate (in shear or elongation) and a characteristic relaxation time of the melt. This is formally known as the Weissenberg number, whereas the Deborah number is a ratio of two time scales, a relaxation time and a...
characteristic time during which molecules experience a certain flow. In the context of the rheological classification scheme, the term Weissenberg number and the symbol \( Wi \) are therefore used throughout this paper. Two time scales were considered by Van Meerveld et al.: the disengagement time, \( t_d \), associated with the reptation process and the Rouse time, \( t_R \), associated with the fast chain retraction mechanism. For each time scale a corresponding Weissenberg number was calculated considering only the longest relaxation times, associated with the longest chains, namely: a Weissenberg number based on the disengagement time \( Wi_d \), and a Weissenberg number based on the Rouse time \( Wi_R \). It was found that when \( Wi_d > 1 \) and \( Wi_R < 1 \), an increase in orientational order occurs leading to an enhancement of point-like nucleation. For \( Wi_d > 1 \) and \( Wi_R > 1 \), the onset of chain stretching occurs. If these conditions are maintained long enough, the stretch of the long chains can exceed a critical value, leading to the growth of oriented crystals (fibrillar regime). This critical stretch was associated with changes in molecular conformation due to rotational isomerization.

**Flow Regimes-Based Models**

From short-term experiments in a duct, Jerschow and Janeschitz-Kriegl\(^{[14]}\) could relate the sizes of the oriented shear and fine-grained layers with the shear rate and shear time. It was found that at the boundary between the fine-grained layer and core \( \gamma_c \), it was constant, with \( \gamma_c \) defined as a critical shear rate, and \( t_s \) the shear time. In the same way the transition to the highly oriented shear layer was characterized by a constant \( \gamma_c \), defined as the shear time. Based on these findings Eder and coworkers\(^{[3,21]}\) proposed a model for flow-induced crystallization in which a critical shear rate acts as a threshold to generate oriented crystalline morphologies. The model consists of a set of differential equations from which the number of flow-induced nuclei, the total shish time, \( t_s \) the total shear time, and the total volume of oriented crystals per unit volume can be obtained. Later, Zuidema et al.\(^{[42]}\) proposed a modified version of the Eder model, the \( S_t \) model, in which molecular orientation and stretch of the longest chains, combined in the second invariant of the deviatoric part of the elastic Finger tensor (equivalent to the often used conformation tensor) \( J_2(B^F_c) \) of the slowest relaxation mode, drives flow-induced crystallization. Only an effect on the creation and growth of fibrillar nuclei was assumed. The nonlinear increase in number density and length of the resulting shish-kebabs as a function of the deformation applied was explained as the result of a self-enhancing process: flow-induced orientation and stretch accelerate both nucleation and longitudinal growth while nuclei locally act as physical crosslinks, increasing the disengagement time, and Rouse time of the longest molecules, thus making them easier to orient and stretch. The effect was modeled as a linear dependence of these relaxation times on the number of flow-induced nuclei. Zuidema et al. tested his model on the experiments of Jerschow et al.\(^{[14]}\) and found that the time integral of \( J_2(B^F_c) \) of the highest relaxation mode remains constant at the transition from spherulitical core to fine-grained layer and to oriented shear layer, corroborating experimental evidences of the dominant role of long chains on flow-induced crystallization in polydisperse melts.

**Motivation**

Most of the studies that deal with morphology development of semi-crystalline polymers upon processing, generally follow an approach that combines experiments with numerical simulations. However, most of the correlations drawn between processing conditions and morphology, e.g., skin layer thickness, are still based on models that lack physical detail, and on experiments performed in injection molding machines. The modeling of such experiments is oversimplified by neglecting the flow history inside the machine during plasticization. Recent findings suggest that even at high temperatures substantial order can be formed and remain in the melt. Azzurri and Alfonso\(^{[43]}\) measured the relaxation of shear-induced nucleation precursors in melts at temperatures slightly above the equilibrium melting temperature and found flow to affect the kinetics of crystallization, even when allowing the melt to relax for a considerable time before cooling it down to crystallization temperature. Furthermore, upon increasing the concentration of long chains in the melt the relaxation times of the nucleation precursors were found to increase. Similar results were found by Vleeshouwers and Meijer\(^{[43]}\). They reported that after short term shearing of iPP at 200 °C, followed by a waiting period of 30 min at 200 °C, the influence of the flow-induced precursors on crystallization was still measurable. Regarding injection molding the implication of these studies is obvious: the complex deformation the material experiences inside the machine before injection is unlikely to be fully erased and therefore its effect on the morphology cannot be neglected. This strongly suggests that morphological studies of semi-crystalline polymers, in first instance should be carried out under conditions in which the initial state of the material is known.

In the present study, we make use of experimental results obtained using two experimental tools, a multipass rheometer (MPR) and a capillary rheometer. Both allow to study crystallization phenomena at high shear rates, but under controlled deformation and thermal histories, which, in contrast to the situation in real injection molding machines, are known a priori. Hence, the influence of flow on crystallization kinetics and developing morphology can be quantified and experimental conditions can be
accurately translated into boundary conditions for numerical simulations. We develop a model for flow-induced crystallization, which revises the underlying ideas of the $S_j$ model and slightly simplifies the recently proposed model by Steenbakkers and Peters to predict the morphology of the oriented crystalline phase. Summarizing, we see the present study as a necessary step to validate the present model by Steenbakkers and Peters, to predict the crystallinity within each spherulite (maximum amount of crystallized material). Expressions for the nucleation density $N(T, p)$ and growth rate $G(T, p)$, yet to be specified, should accurately describe the temperature and pressure dependence of the quiescent crystallization kinetics.

### Modeling Crystallization

Under the combined effect of cooling and flow-induced molecular deformation, the resulting material morphology upon crystallization combines both spherulitical and fibrillar oriented structures. Both have to be taken into account if a realistic description of the final morphology is envisaged.

#### Quiescent Crystallization

Spherulitical structures develop under quiescent conditions, their number and size depending on the cooling history and on the concentration of nucleating agents. To model this we use the Schneider rate equations, which provide a complete picture of the morphology, in terms of number of spherulites, their radius, surface and volume, and consist of a set of nested differential equations that reads

\[ \phi_3 = 8\pi N \quad (\phi_3 = 8\pi N), \]

\[ \phi_2 = G\phi_3 \quad (\phi_2 = 8\pi R_{\text{tot}}), \]

\[ \phi_1 = G\phi_2 \quad (\phi_1 = S_{\text{tot}}), \]

\[ \phi_0 = G\phi_2 \quad (\phi_0 = V_{\text{tot}}), \]

in which $\phi_0$ is the undisturbed total volume $V_{\text{tot}}$ of the spherulites per unit volume, $\phi_1$ is the total surface $S_{\text{tot}}$ of the spherulites per unit volume, $\phi_2$ is $8\pi$ times the sum of the radii $R_{\text{tot}}$ of the spherulites per unit volume, $\phi_3$ is $8\pi$ times the number of the spherulites $N$ per unit volume, $N = N(T, p)$ is the nucleation rate and $G = G(T, p)$ the crystal growth rate. In order to correct for impingement, different models can be employed, the most widespread being the Kolmogorov–Avrami model,

\[ -\ln\left(1 - \xi_j\right) = \phi_0. \]

The degree of crystallinity $\xi$ can be obtained by multiplying the degree of space filling $\xi_j$ with the degree of crystallinity within each spherulite (maximum amount of crystallized material). Expressions for the nucleation density $N(T, p)$ and growth rate $G(T, p)$, yet to be specified, should accurately describe the temperature and pressure dependence of the quiescent crystallization kinetics.

### Modeling Flow Effects on Crystallization

The ideas contained in the model proposed by Zuidema et al. and in the recent model developed by Steenbakkers and Peters for flow-induced crystallization, are here combined and adapted in a model suitable for implementation in industrially relevant flow simulations, yet offering detailed predictions of morphological features.

We start by considering the total number of nuclei $N$ to be the result of heterogeneous (athermally activated) quiescent nuclei, $N_p$, and homogeneous (sporadically created) flow-induced nuclei, $N_f$.

\[ N = N_p + N_f. \]

The quiescent nucleation rate is thus a function of temperature and pressure only,

\[ \dot{N}_p = T \frac{\partial N_p}{\partial T} + p \frac{\partial N_p}{\partial p}. \]

The temperature and pressure dependence of $N_p$ is given in Equation (28) and (29) for the material studied here. The flow-induced nucleation rate is assumed to be a function of the stretch of the longest chains present in the melt. This seems in contradiction with the work of Van Meerveld et al. who showed that pointlike nucleation is already accelerated for $Wi_k > 1$ and $Wi_k < 1$. However, due to the coupling of $\tau_d$ with $\tau_k$ with $N_f$, these Weissenberg numbers, based on the initial relaxation times, are not representative for the long chains driving the nucleation process. Especially for long flow times, the classification scheme should therefore be used with care. Related to this is the observation of Housmans et al. that the transition to oriented crystallization occurs at a critical amount of work, as reported earlier by Mykhaylyk et al. but that this critical work decreases for longer flow times. It is envisioned that the stretch of the high-end tail of the molecular weight distribution increases the number of aligned chain segments whose conformation is closer to the crystalline state. Based on this idea, the flow-enhanced nucleation rate was modeled by Steenbakkers and Peters using a fourth-order dependence on the molecular stretch of the slowest relaxation mode only.
\[ \dot{N}_f = g_n (\Lambda^4 - 1), \]  

in which \( g_n \) is a scaling parameter that depends on temperature only. Recently, Graham and Olmsted\(^{[47]} \) simulated anisotropic nucleation based on the configuration of chains, obtained from an advanced molecular rheological model (the GLaMM model\(^{[46]} \)), via coarse-grained kinetic Monte Carlo simulations. They found an exponential dependency on the molecular stretch that, for stretch values up to about 3.5, can be described equally well by the fourth-order dependence used here. It should be noted that the model of Graham and Olmsted does not contain any effect of the nuclei on the rheology of the melt.

Some experimental observations have been reported that a saturation limit exists beyond which the rate of flow-induced nucleation becomes zero.\(^{[49]} \) Hristova and Peters\(^{[50]} \) measured the number of flow-induced nuclei in iPP HD120MO as a function of shear rate in a Linkam shear cell. These data indicate a saturation level of the total number of flow-induced nuclei, \( N_{f,max} \), independent of the shear rate. Housmans et al.\(^{[45]} \) studied saturation in the same material as well as two other iPPs under shear. They observed an increase in the saturation level as a function of shear rate, but this effect seemed to level off at higher shear rates. Steenbakkers and Peters\(^{[44]} \) modified Equation (8) to include saturation as follows,

\[ \dot{N}_f = g_n (\Lambda^4 - 1) \left[ 1 - \frac{N_f}{N_{f,max}} \right]. \]  

Graham and Olmsted\(^{[47]} \) calculated the “instantaneous nucleation rate” (the term containing the stretch dependence) from their simulations in a way analogous to Equation (9).

Following the approach of Zuidema et al.\(^{[42]} \) the flow-induced nuclei are assumed to act as physical crosslinks in the melt and the relaxation times of the high molecular weight (HMW) chains in the melt are made a linear function of the number of flow-induced nuclei,

\[ \tau_j = a_T \tau_{Rj} (1 + \alpha N_f), \]  

in which \( j \in \{ d, R \} \) refers to the disengagement or Rouse time of the slowest mode and \( \alpha \) is a coupling parameter, which expresses the creation of physical crosslinks in the melt. However, this coupling requires some caution, since, as will be shown in Section 5, it makes it almost impossible to relax the orientation and stretch of these molecules, with the consequence of flow-induced crystallization proceeding up to unrealistic time scales. To circumvent this, we introduce a pre-factor \( \delta \) in Equation (9), which sets the rate of flow-induced nucleation to zero if the flow is stopped. In this way, the present model mimics the model of Steenbakkers and Peters\(^{[44]} \) in which nucleation precursors are created during flow, but only nucleate after cessation of flow. The creation of precursors is described by an expression similar to Equation (9) and the relaxation time is related to the number of flow-induced precursors analogous to Equation (10). This was based on experimental observations that, in short term shear flows under isothermal conditions, all spherulites have nearly the same size, indicating that they start to grow around the same time. Because the nucleation of precursors after flow occurs instantaneously, and the nuclei are treated as particles rather than physical crosslinks, the creation of precursors mainly takes place during flow in the model of Steenbakkers and Peters. If flow-induced nucleation would continue after the flow, one would expect a distribution in sizes of flow-induced crystals. In the present, simplified version of the model, the final equation for flow-induced nucleation reads

\[ \dot{N}_f = \delta g_n (\Lambda^4 - 1) \left[ 1 - \frac{N_f}{N_{f,max}} \right] \]  

with

\[ \delta = \begin{cases} 1 & \text{if } \gamma \neq 0 \\ 0 & \text{if } \gamma = 0 \end{cases} \]  

Both quiescent and flow-induced point-like nuclei grow radially, therefore the total number of nuclei \( N \) appears in Equation (1).

Thus, at an early stage, flow-induced nuclei are envisioned as spheres whose number will depend on the flow conditions. A model for the growth of point-like nuclei into fibrillar nuclei is developed next. Based on the experimental evidences that a threshold stress needs to be surpassed to change from the isotropic to the oriented crystallization regime\(^{[35]} \) and that this is associated with stretching the long chains beyond a minimum value allowing rotational isomerization,\(^{[41]} \) we introduce a critical stretch \( \Lambda_{crit} \) above which fibrillar growth occurs. Since theoretical or experimental values for the critical
chains, in terms of orientation and stretch is here assumed to influence the growth rate. Accordingly, we write the shish-growth rate equation \( L \) as

\[
L = \begin{cases} 
0 & \text{if } \Lambda \leq \Lambda_{\text{crit}} \\
g_j J_2 \left( B_{e,\text{avg}} \right) & \text{if } \Lambda > \Lambda_{\text{crit}} 
\end{cases}
\]  

(13)

where \( J_2 \left( B_{e,\text{avg}} \right) \) is the second invariant of the deviatoric elastic Finger tensor of a mode, representative of the whole molecular weight distribution, which is added to the slow mode. The disengagement time of this mode is calculated by

\[
\tau_{\text{d,avg}} = \sum G_i \tau_i^R \sum \frac{G_i \tau_i}{
\]  

(14)

which is the viscosity average over the linear viscoelastic relaxation spectrum. Thus, a two-mode model is used, in which one mode represents the long chains and the other an average contribution of all chains. In Equation (13), \( g_j \) is a scaling parameter for the influence of \( J_2 \) on the thread-like growth of the nuclei. By considering an average relaxation time of the melt relaxation spectrum, we assume the growth of a shish to be a process in which all molecular chains participate, favored by the combined effect of molecular stretch and orientation, which is conveniently expressed by \( J_2 \left( B_{e,\text{avg}} \right) \). From the growth rate of shish it is possible to calculate the total undisturbed length, surface, and volume per unit volume, employing the rate equations of Eder,\textsuperscript{[3]} which read

\[
\dot{\psi}_3 = 8\pi N_t \quad \left[ N_t \text{ given by Equation (11)} \right],
\]  

(15)

\[
\dot{\psi}_2 = 4\pi N_t \dot{L} \quad \left[ \dot{L} \text{ given by Equation (13)} \right],
\]  

(16)

\[
\dot{\psi}_1 = G \psi_2 \quad \left( \psi_1 = S_{\text{tot}} \right),
\]  

(17)

\[
\dot{\psi}_0 = G \psi_1 \quad \left( \psi_0 = V_{\text{tot}} \right),
\]  

(18)

in which \( \psi_0 \) is the total volume of shish-kebabs per unit volume, \( \psi_1 \) the total surface \( S_{\text{tot}} \) of the shish-kebabs per unit volume, \( \psi_2 \) is 4\pi times the total length \( L_{\text{tot}} \) of the shish per unit of volume, and \( \psi_3 \) is 8\pi times the total number of flow-induced nuclei per unit volume. Since the model gives the undisturbed spherulitical and oriented crystalline volume, \( \psi_0 \) and \( \psi_0 \), respectively, we need to correct for impingement. We adopt the Kolmogorov–Avrami model, Equation (5), to take into account the contribution of both spherulitical and oriented crystalline structures. The
modified model reads

\[-\ln\left(1 - \xi_g\right) = \phi_0 + \psi_0. \tag{19}\]

The scaling parameters \(g_n\) and \(g_t\) are made temperature dependent according to time temperature superposition. Hence, at a certain temperature they are shifted with \(\alpha_t\) to a reference temperature,

\[g_n(T) = \alpha_t(T, T_0)g_{n0}, \tag{20}\]
\[g_t(T) = \alpha_t(T, T_0)g_{t0}. \tag{21}\]

The real number and total length of flow-induced nuclei per unit volume, taking into account impingement, can be found by solving the following equations:

\[N_{f,\text{real}} = \delta g_n \left(\Lambda^4 - 1\right) \left[1 - \frac{N_f}{N_{f,\text{max}}} \right] \left(1 - \xi_g\right), \tag{22}\]

and

\[L_{\text{tot,real}} = \begin{cases} N_{f,\text{real}} g_n b_{\text{avg}}^d \left(B_{e,\text{avg}}^d \right)^3 \left(1 - \xi_g\right) & \text{if } \Lambda \leq \Lambda_{\text{crit}} \\ N_{f,\text{real}} g_n b_{\text{avg}} \left(B_{e} \right)^3 \left(1 - \xi_g\right) & \text{if } \Lambda > \Lambda_{\text{crit}} \end{cases} \tag{23}\]

in which \(N_{f,\text{real}}\) denotes the real number of flow-induced nuclei per unit volume and \(L_{\text{tot,real}}\) the real total shish length per unit volume.

### Stress Problem

The Rolie-Poly model\[^{[51]}\] is used to calculate the part of the nonlinear viscoelastic response, necessary to solve the flow-induced crystallization problem. Namely, the stretch of the longest chains in the melt \(\Lambda_{\text{HMW}}\) and the second invariant of the deviatoric part of the elastic Finger tensor of the viscosity-averaged mode \(J_2\left(B_{e,\text{avg}}^d\right)\). The Rolie-Poly model was developed for the rheology of linear polymers and results of the model show a good agreement with rheological measurements in steady and transient regimes in both shear and extension flows. The model is of the differential type and its single-mode version reads

\[\frac{B_{e}^d}{\tau_d} + \frac{1}{\tau_d} \left(B_{e} - I\right) + 2 \left(1 - \sqrt{3/\left(\text{tr}(B_{e})\right)}\right) \left(\frac{B_{e} + \beta \left(\frac{\text{tr}(B_{e})}{3}\right) \left(B_{e} - I\right)}{\tau_r}\right) = 0. \tag{24}\]

in which \(B_{e}\) is the elastic Finger, or conformation, tensor. Its deviatoric part follows from

\[B_{e}^d = B_{e} - \frac{1}{3} \text{tr}(B_{e}) I \tag{25}\]

and the molecular stretch \(\Lambda\) follows from:

\[\Lambda = \sqrt{\frac{\text{tr}(B_{e})}{3}}. \tag{26}\]

Each term of Equation (24) addresses a specific molecular mechanism, such as chain reptation, chain stretch relaxation, and convective constraint release, which makes this model particularly physically intuitive.\[^{[51]}\] In the model two time scales are of importance: \(\tau_d\), the disengagement (reptation) times, and the Rouse (stretching) times \(\tau_{\text{R,}i}\). Besides the Rouse times \(\tau_{\text{R,}i}\), this model contains two nonlinear parameters, governing the stretch dependence of relaxation via convective constraint release, a pre-factor \(\beta \in [0, 1]\) and an exponent \(\delta < 0\); see Equation (24). For higher strain rates the Rolie-Poly model, in its single-mode form, produces a faster stress growth when compared to the GLaMM model,\[^{[48]}\] on which it was based.\[^{[51]}\] The explanation, given by the authors, is that the full theory contains a spectrum of stretch relaxation times, reflecting different parts of the chain, whereas the Rolie-Poly model assumes uniform stretch. To compensate for the overprediction of the steady-state stress at large rates, the authors advised to set \(\beta = 0\). We follow this advice.

### Material and Experimental Methods

#### Material Selection

The research conducted on flow-induced crystallization in our group has been restricted to a small number of materials such that extensive material data, obtained from rheological measurements and crystallization studies, could be collected. Obviously, for modeling purposes in studies that aim at morphology prediction, the availability of extensive material data is crucial. In this study, we restrict ourselves to a purely linear iPP (grade HD120MO, Borealis) which was studied previously,\[^{[1,2,15,44,45,50,52]}\] yielding molecular weight related properties and the differential scanning calorimetry (DSC)-measured melting temperature, see

<table>
<thead>
<tr>
<th>Grade</th>
<th>(M_{w}) (kg mol(^{-1}))</th>
<th>(M_w/M_n)</th>
<th>(T_m) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HD120MO</td>
<td>365</td>
<td>5.4</td>
<td>163</td>
</tr>
</tbody>
</table>

Table 1. Physical properties of iPP HD120MO.
Table 2. Thermal properties of iPP HD120MO.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c_p$</td>
<td>3175.3 J·kg$^{-1}$·K$^{-1}$</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>0.11 W·m$^{-1}$·K$^{-1}$</td>
</tr>
</tbody>
</table>

Table 1. The thermal properties of iPP HD120MO, taken from the Moldflow material database, are assumed to be constants and are listed in Table 2.

Quiescent Crystallization Kinetics in Isotactic Poly(propylene) (iPP) HD120MO

Van der Beek[15,16] performed quiescent crystallization experiments in a dilatometer, measuring the specific volume of iPP HD120MO for different cooling rates at a pressure of 40 MPa. He could predict the evolution of the specific volume measured during cooling, using the Schneider rate equations and a state equation in which the dependence of density on the volume fraction of crystalline and amorphous material was taken into account. The spherulitical growth rate $G(T)$ and the number of nuclei per unit volume $N_0(T)$ were determined from polarized optical microscopy experiments. To describe specific volume at elevated pressures, both $G(T)$ and $N_0(T)$ were adapted in the following way:

$$G(T, p) = G_{\text{max}} \exp \left[ -b(T - T_{\text{ref}} - f_g(p))^2 \right], \quad \text{(27)}$$

$$N_0(T, p) = 10^{n_0 + n_1(T - f_1(p))}, \quad \text{(28)}$$

where

$$f_i = p \alpha \Delta p + p n_2 \Delta p^2 \quad i = g, n, \quad \text{(29)}$$

$$\Delta p = p - p_{\text{ref}}. \quad \text{(30)}$$

The parameters used in Equation (27–29) are taken from[25] and given in Table 3. Only for the highest cooling rate used (32.5 °C·s$^{-1}$) the model gave a poor result. Such limitations are well known, see for example Lamberti and Naddeo[53] and De Santis et al.[54] where an enhanced nucleation model, depending on the cooling rate, was proposed. This issue needs more attention in future studies. The nucleation curve and the growth rate curve at atmospheric pressure are given in Figure 3(a) and (b), respectively.

Regarding the heat of crystallization $H_i$, from the literature it is known that for iPP the value lies between 170 and 273 kJ·kg$^{-1}$ for a pure crystal. In this study, we take it to be 170 kJ·kg$^{-1}$. The degree of crystallinity $\xi$ is found by multiplying the degree of space

$$\xi \text{ (at } T_{\text{ref}}) = \frac{V_i}{V_{g0}} \frac{V_g}{V_{g0}}, \quad \text{(31)}$$

Table 3. Model parameters for the spherulitical growth rate $G(T, p)$ and effective number of nuclei $N(T, p)$ for iPP (HD120MO, Borealis).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$G_{\text{max}}$</td>
<td>$2.9669 \times 10^{-6}$ m·s$^{-1}$</td>
</tr>
<tr>
<td>$b$</td>
<td>$1.3000 \times 10^{-3}$ °C$^{-1}$</td>
</tr>
<tr>
<td>$T_{\text{ref}}$</td>
<td>$9.00 \times 10^1$ °C</td>
</tr>
<tr>
<td>$p_{g0}$</td>
<td>$7.0333 \times 10^{-8}$ K·Pa$^{-1}$</td>
</tr>
<tr>
<td>$p_{g1}$</td>
<td>$-4.7000 \times 10^{-15}$ K·Pa$^{-2}$</td>
</tr>
<tr>
<td>$p_n0$</td>
<td>$3.00 \times 0$ K·Pa$^{-2}$</td>
</tr>
<tr>
<td>$n_0$</td>
<td>$1.00 \times 10^5$ log(m$^{-3}$)</td>
</tr>
<tr>
<td>$n_1$</td>
<td>$-4.90 \times 10^{-2}$ log(m$^{-3}$·K$^{-1}$)</td>
</tr>
<tr>
<td>$p_{\text{ref}}$</td>
<td>$1.00 \times 10^5$ Pa</td>
</tr>
</tbody>
</table>

Figure 3. (a) Quiescent nucleation rate $N_0(T)$ curve. (b) Spherulitical growth rate $G(T)$ curve.
rates are much higher in the regions of interest, i.e., the outer layers of the samples where the fine-grained and oriented morphologies develop. Therefore the assumption of shear rate independence of $N_{f,\text{max}}$ is justified. Since its temperature dependence is unknown, we use the value at $T = 135 \, ^\circ\text{C}$[50] for all temperatures. It is clear that the model can be improved at this point, especially for the non-isothermal capillary flows.

To determine the shish growth parameter $g_{l0}$ and the critical stretch $L_{\text{crit}}$, the flow-induced crystallization model is combined with a linear viscoelastic model for a suspension of spheres and cylinders[56] and applied to the rheological measurements of Housmans et al.[45] after short-term shear flow. Figure 4 shows that for $g_{l0} = 1.0 \times 10^{-7} \, \text{m} \cdot \text{s}^{-1}$ and $L_{\text{crit}} = 40$, the onset time of the increase in $G(t)$ is captured for three of the four shear times at a shear rate $\dot{\gamma} = 30 \, \text{s}^{-1}$, but is overpredicted for the shortest shear time. The shape of $G(t)$ corresponds reasonably well with the experimental curves. For the three longest shear times, the calculations end at $\xi = 0.9999$. The behavior up to full space filling can be seen in the curve for the shortest shear time. The calculated loss modulus, not depicted here, shows oscillations at high degrees of space filling. This is an artefact of the suspension model, see also Steenbakkers and Peters[56] and Housmans et al.[45]. The onset times are captured just as well as in the case of the storage modulus.

### Viscoelastic Material Data

The rheological properties at a temperature of 190 °C are given in Table 4. The linear viscoelastic behavior of the material is described by a seven-mode discrete Maxwell relaxation time spectrum,

$$G'(\omega) = \sum_{i} g_i \frac{\omega^2 \tau_i^2}{1 + \omega^2 \tau_i^2}, \quad (31)$$

$$G''(\omega) = \sum_{i} g_i \frac{\omega \tau_i}{1 + \omega^2 \tau_i^2}, \quad (32)$$

where $G'$ and $G''$ are the storage and the loss modulus, respectively. The set of relaxation moduli, $g_i$ and times, $\tau_i$, were determined elsewhere.[52] The temperature

<table>
<thead>
<tr>
<th>$T$</th>
<th>$a_T$</th>
<th>$b_T$</th>
</tr>
</thead>
<tbody>
<tr>
<td>°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shift factors</td>
<td>135</td>
<td>4.944</td>
</tr>
<tr>
<td></td>
<td>145</td>
<td>3.579</td>
</tr>
<tr>
<td></td>
<td>155</td>
<td>2.557</td>
</tr>
<tr>
<td></td>
<td>165</td>
<td>1.894</td>
</tr>
<tr>
<td></td>
<td>175</td>
<td>1.328</td>
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<tr>
<td></td>
<td>190</td>
<td>1.000</td>
</tr>
<tr>
<td></td>
<td>205</td>
<td>0.760</td>
</tr>
<tr>
<td></td>
<td>220</td>
<td>0.584</td>
</tr>
<tr>
<td></td>
<td>235</td>
<td>0.472</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>0.358</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mode</th>
<th>$g_i$</th>
<th>$\tau_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$10^4 , \text{Pa} \cdot \text{s}$</td>
<td>s</td>
</tr>
<tr>
<td>Maxwell</td>
<td>9.0200</td>
<td>0.002</td>
</tr>
<tr>
<td></td>
<td>4.2100</td>
<td>0.010</td>
</tr>
<tr>
<td></td>
<td>1.8200</td>
<td>0.051</td>
</tr>
<tr>
<td></td>
<td>0.5620</td>
<td>0.258</td>
</tr>
<tr>
<td></td>
<td>0.0878</td>
<td>1.300</td>
</tr>
<tr>
<td></td>
<td>0.0109</td>
<td>6.580</td>
</tr>
<tr>
<td></td>
<td>0.0075</td>
<td>33.200</td>
</tr>
<tr>
<td>Cross</td>
<td>4.8489 $\times 10^3$</td>
<td>0.2674</td>
</tr>
</tbody>
</table>

Figure 4. Calculated (solid lines) and measured (dashed lines) storage modulus after different shear flows ($\dot{\gamma} = 30 \, \text{s}^{-1}$ and $t_s = 2, 5, 6, \text{and} 7 \, \text{s}$) at 138 °C, in ref.[45]
dependence of the horizontal ($a_h$) and vertical ($b_v$) shift factors is described using the WLF equation,
\[
\log a_h(T, T_0) = \frac{-C_1(T - T_0)}{C_2 + T - T_0},
\]
and a Cross model\[^{57}\] is used to describe the temperature and shear rate dependence of the viscosity,
\[
\eta(T, \dot{\gamma}) = \frac{a(T, T_0)\eta_0(T_0)}{1 + (a(T, T_0)\eta_0(T_0))^{1/(1-n)}}.
\]
Using the viscoelastic data listed in Table 4 we find the viscosity-averaged relaxation time $\tau_{d,avg}$ given by Equation (14), equal to 12.2 s at $T = 190^\circ$C.

Uniaxial viscosity measurements, supplied by Borealis, are used to determine the Rouse times. This is done by fitting a multi-mode Rolie-Poly model to the data. The main feature in uniaxial extension, namely strain hardening, is closely related to the stretching dynamics. Therefore, these experiments are very well suited to obtain the Rouse times. The strain rates $\dot{\varepsilon} = 0.3$ s\(^{-1}\), $\dot{\varepsilon} = 1$ s\(^{-1}\), $\dot{\varepsilon} = 3$ s\(^{-1}\), and $\dot{\varepsilon} = 10$ s\(^{-1}\) were applied at a constant temperature, $T = 180^\circ$C.

As stated before, flow-enhanced nucleation rates can be described well by a fourth-order dependence on the stretch of the slowest mode only, see Equation (8). Since the molecular conformations of different modes in the Rolie-Poly model are not coupled, only the dynamics of the slowest mode itself contributes to flow-enhanced nucleation. Therefore, although the uniaxial viscosity data can be fitted by different sets of Rouse times, we are only interested in obtaining a unique value for the longest Rouse time, $\tau_R$. This is accomplished by using the non-stretching Rolie-Poly equation for all modes except for the slowest. The only remaining free parameter is then found by fitting the model to the data for the two lowest strain rates: $\tau_R = 2.49$ s. The shorter Rouse times can be found by adding stretching modes and including the uniaxial viscosity data for higher strain rates.

The Rouse time of the viscosity-averaged relaxation mode $\tau_{R,avg}$ can be estimated with the expression proposed in\[^{38}\], which in the case of the average mode reads
\[
\tau_{R,avg} = \frac{\tau_{d,avg}}{Z},
\]
in which $Z$, the number of entanglements per chain, can be calculated from the weight averaged molecular weight $M_w$ and the averaged molar mass between entanglements $M_e$,
\[
Z = \frac{M_w}{M_e}.
\]
From\[^{41}\] we took $M_e = 5.5$ kg mol\(^{-1}\) and find $\tau_{R,avg} = 6.1 \times 10^{-2}$ s.

**Morphology Development Under Quasi-Isothermal Conditions—the Multipass Rheometer (MPR)**

Recently a modified MPR based on the original device developed in the group of Mackley\[^{59}\] was proposed by Housmans et al.\[^{1}\]. In Figure 5(a) a schematic representation of the MPR is given. The pistons “A” are driven by means of hydraulics that are not shown here. The MPR can incorporate different flow geometries and allows in situ studies on the kinetics of flow-induced crystallization and its relation to the crystalline morphology, under a controlled thermal-mechanical history. Both steady and small and large amplitude oscillatory shear flows can be generated. Additionally, the double-piston configuration allows to study advanced injection molding processes, such as Push–Pull\[^{60}\] and Scorim\[^{61}\] in which by reversing the flow inside the mold cavity during cooling, material solidification takes place under a continuous shear field.

In this study, we focus on the experiments reported in ref\[^{5}\] in which the MPR is equipped with a slit geometry of 120 mm $\times$ 6 mm $\times$ 1.5 mm. The material is held above its equilibrium melting temperature at 220 $^\circ$C for 10 min, and subsequently cooled down to the desired temperature at which flow is applied. Such a protocol has the purpose of erasing any deformation history prior to the flow. The flow time, $t_f$, is restricted to prevent material that passed through the contraction region between the cylinder and the slit.

![Figure 5](image-url)
from reaching the view point. Thus, entrance effects are excluded from the analysis. The flow time should satisfy

$$ t_f < \frac{0.5L}{v_{max}}, $$

in which $L$ is the slit length and $v_{max}$ is the maximum velocity inside the slit, which, for a Newtonian fluid behavior, is estimated by $v_{max} = 1.5v_{avg}$, in which the average velocity is prescribed for each experiment. The different flow conditions used are listed in Table 5.

### Table 5. Flow conditions for the MPR experiments.

<table>
<thead>
<tr>
<th>Conditions</th>
<th>$t_{flow}$</th>
<th>$v_{avg}$</th>
<th>$T_{flow}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MPR1</td>
<td>0.1875</td>
<td>0.2</td>
<td>165</td>
</tr>
<tr>
<td>MPR2</td>
<td>0.375</td>
<td>0.1</td>
<td>145</td>
</tr>
<tr>
<td>MPR3</td>
<td>0.375</td>
<td>0.1</td>
<td>165</td>
</tr>
<tr>
<td>MPR4</td>
<td>3.0</td>
<td>0.0125</td>
<td>145</td>
</tr>
</tbody>
</table>

Morphology Development Under Non-Isothermal Conditions—the Capillary Rheometer

A capillary rheometer resembles early injection molding machines that employed, instead of a reciprocating screw, a plunger to pressurize, and push the melt into a mold. Capillary rheometers are designed to measure the rheological properties of polymer melts at high shear rates, forcing the melt to flow into a capillary or a slit geometry. Since the material is homogeneously molten inside a cylinder under no-flow conditions, a uniform thermal-mechanical history is attained before injection. In ref.[2] a capillary rheometer (Rheograph 6000, Göttfert Werkstoff-Prüfmachinen GmbH, Germany) was adapted to make it perform as an injection molding machine, by adding a rectangular cavity of dimensions $2\text{ mm} \times 12\text{ mm} \times 135\text{ mm}$, see Figure 5(b). A cooling clamp is used to thermostatically cool the mold walls. We consider the modeling of experiments using the capillary rheometer as a necessary step in between the MPR and an injection molding machine, since the experiments are conducted under non-isothermal conditions and the developed flow field is, like in injection molding, spatially inhomogeneous: behind the flow front, kinematics are shear dominated but near the flow front, due to the fountain flow, significant extension takes place. The post-filling stages of injection molding, in which pressure levels are high and the fluid velocity inside the cavity is low, cannot be mimicked yet by the capillary mold and thus their effect on the morphological development is disregarded here. The effect of varying injection speed is assessed using the different flow speeds summarized in Table 6. For all conditions the injection temperature and the temperature at the slit walls are set to 220 and 80 $\text{oC}$, respectively.

### Table 6. Flow conditions for the capillary rheometer experiments.

<table>
<thead>
<tr>
<th>Conditions</th>
<th>$t_{flow}$</th>
<th>$v_{avg}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CA1</td>
<td>2</td>
<td>0.126</td>
</tr>
<tr>
<td>CA2</td>
<td>4</td>
<td>0.0662</td>
</tr>
<tr>
<td>CA3</td>
<td>8</td>
<td>0.03758</td>
</tr>
</tbody>
</table>

#### Morphology Characterization

Multipass Rheometer (MPR) experiments

The morphology of the MPR samples is characterized ex situ via polarized optical light microscopy. Micrographs are taken from thin cross sections of $3-7\text{ µm}$, microtomed at $-130\text{ °C}$ in the vorticity plane, under crossed polarizers rotated $\pm 45\text{°}$ with respect to the flow direction. The cross-sections are taken from the center of the slit, see Figure 6.

Only the samples processed at the highest flow speed conditions, MPR1 and MPR2, develop an oriented shear layer followed by a fine-grained layer, see Figure 7.

Figure 6. Layout procedure to microtome samples for optical light microscopy.
Furthermore, the lower flow temperature of condition MPR2 significantly increases the thickness of the oriented layer. For the conditions MPR3 and MPR4 there is no development of oriented layers, only a fine-grained layer is found. For the condition MPR4 the morphological gradient across the thickness is very smooth, denoting a linear decrease in the size of spherulites toward the walls and a pronounced effect of transcrystallinity. The thicknesses of the oriented and fine-grained layers are given in Table 7 for all the conditions.

Capillary Rheometer Experiments

Samples are microtomed according to the same procedure explained for the MPR at three different positions along the length of the slit: close to the gate, at the middle, and close to the end of the slit, see Figure 6. The micrographs for the different flow conditions are given in Figure 8. For all flow conditions the morphology is inhomogeneous, exhibiting a layer type of structure with a highly oriented crystalline region. Four different layers are identified from the edge to the core: a thin skin layer, a transition layer, and a shear layer, followed by an isotropic core, see Figure 9.

In all samples the thickness of the oriented region, composed by the skin, transition, and shear layers, increases toward the middle of the slit and decreases again toward the end of the slit, see Figure 10. Such variation is explained by the thermal and mechanical deformation experienced by the material. The skin layer, which originates from the deposition of stretched material in the flow front (fountain flow), i.e., subsequently quenched at the walls, remains constant along the slit length. However, thickness of the transition and shear layers result from the combined effect of cooling and shear deformation. Close to the gate the injection of molten material keeps the temperature relatively high, favoring the relaxation of orientation. At the middle of the slit, the material experiences a longer thermal and shear deformation history, which is reflected in the thicker oriented layers. The material that fills the end of the slit channel travels through the core region at low shear rates experiencing a short cooling and mechanical history, thus the thickness of the oriented layers decreases toward the end of the slit. The increase in injection speed results in thinner oriented layers due to the larger amount of heat convected inside the slit per unit time as well as the higher contribution from viscous dissipation, which, combined, cause a lower cooling rate. Therefore, the transition from oriented crystalline layers to spherulitical core is shifted toward the walls. Moreover, the cooling time during filling is also obviously decreased. Hence, at higher injection speeds the shorter relaxation times that result from lower cooling rates and shorter cooling times during filling explain the decrease in thickness of the oriented crystalline layers.

Computation of the Flow Kinematics

Viscous Flow Problem

The governing equations required to model the experiments of the MPR and capillary rheometer are presented. We consider the flow to be incompressible and inertial effects negligible, yielding an incompressible Stokes flow problem. Thus the continuity and momentum equations read

$$\nabla \cdot \mathbf{u} = 0, \quad (38)$$

$$\nabla p = \nabla \cdot \tau, \quad (39)$$

where $\mathbf{u}$ is the velocity field, $\tau$ the extra stress tensor, and $p$ denotes the pressure. The latent heat of crystallization is incorporated as a source term, $\rho H \dot{\xi}$, in the energy equation, with $H$ the heat of crystallization and $\dot{\xi}$ the rate of change of the degree of crystallinity. Heat conduction is described

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Oriented layer (mm)</th>
<th>Fine-grained layer (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MPR1</td>
<td>0.07</td>
<td>0.20</td>
</tr>
<tr>
<td>MPR2</td>
<td>0.16</td>
<td>0.25</td>
</tr>
<tr>
<td>MPR3</td>
<td>–</td>
<td>0.20</td>
</tr>
<tr>
<td>MPR4</td>
<td>–</td>
<td>0.10</td>
</tr>
</tbody>
</table>
by Fourier’s law with an isotropic heat conduction coefficient given in Table 2. Neglecting thermal radiation and assuming compression effects to be negligible, the energy balance reads

\[ \rho c_p \dot{T} = 2\eta \mathbf{D} : \mathbf{D} + \nabla (\lambda \nabla T) + \rho H \dot{\varepsilon}, \]

(40)

where \( \mathbf{D} \) is the rate of deformation tensor and \( \eta \) the viscosity.

The flow kinematics are thus assumed to be determined by the kinematic boundary conditions and a generalized Newtonian description is adopted. Since we take into account the hardening effect of the crystalline structures on the viscosity, viscosity is here made dependent on temperature, the deviatoric part of the rate of deformation tensor \( \mathbf{D} \) and space filling \( \xi_g \).

\[ \eta = \eta \left( T, \mathbf{D}^d, \xi_g \right). \]

(41)

According to the generalized Newtonian flow description, the extra stress tensor \( \tau \) then reads

\[ \tau = 2\eta \left( T, \mathbf{D}^d, \xi_g \right) \mathbf{D}. \]

(42)

The viscosity dependence on temperature and shear rate is described by the Cross model, Equation (34). The values of the model parameters and the WLF constants, see Equation (33), are listed in Table 4.

Crystallization Effects on the Flow

The growth of crystalline structures increases the melt viscosity (hardening), and during the filling stage this effect can become important. Lamberti et al.\(^{[62]}\) gave a review on experimental studies concerning the viscosity hardening of polymer melts during crystallization. A list of available models to describe changes in rheology with the increase in crystallinity was given, distinguishing suspension-based from empirical models. The numerous different models illustrate the lack of understanding how crystallization kinetics and structural changes determine the viscosity hardening evolution. The authors proposed a new experimental method that combines DSC and rheometry, to determine the change in viscosity induced by the degree of space filling \( \xi_g \). They found that the influence of crystallinity on viscosity can be described by a shift factor, \( \alpha_\xi (\xi_g) \), which is equivalent to adopting a time-hardening superposition. Hence, the viscosity is shifted according to the temperature and degree of space filling.

The effect of shear flow on the rheology of viscoelastic suspensions filled with rigid particles was analyzed by Hwang et al.\(^{[63]}\) using advanced finite element methods, however their method was limited to 2-D flows. Despite the
usefulness of such analyses in providing a more comprehensive insight into the rheological phenomena involved, they are computationally very expensive. This is certainly true when going to 3-D simulations.\textsuperscript{[64,65]} Thus, simple suspension models that can relate rheological properties of melts with the underlying crystalline morphology are more attractive to implement in injection molding codes. In a recent publication\textsuperscript{[56]} early work on suspension modeling was reviewed and a generalized self-consistent method\textsuperscript{[66]} was applied to describe the evolution of linear viscoelastic properties of crystallizing melts. The model allows to incorporate particles with different shapes, discriminating oriented from unoriented crystals. Spherulites are represented by spheres and shish-kebabs by cylinders. Additionally, the mechanical properties of the particles and the matrix are transient and dependent on the ongoing microstructural changes. The approach of Lamberti et al.\textsuperscript{[62]} is more simple; crystalline particles are assumed rigid and only space filling is accounted for, i.e., no influence of oriented structures.

Here, we follow the model proposed in ref.\textsuperscript{[62]} in which viscosity is shifted according to the computed degree of space filling $\xi_g$. The generalized Newtonian viscosity then becomes:

$$\eta = \eta(T, \gamma, \xi_g) = \eta_0(\gamma \sigma a_i) a_i a_i,$$

(43)

with the shift factor $a_i$ given by:

$$a_i(\xi_g) = 10^{a b \xi_g},$$

(44)

where $a$ and $b$ are defined as hardening parameters. The authors used their model to describe experiments conducted with an iPP ($M_w = 350$ kg mol$^{-1}$, $M_w/M_n = 5.3$), very similar to iPP HD120MO, see Table 1, and found $a = 3.875$ and $b = 1.236$. The evolution of the viscosity hardening shift factor $a_i$ with the degree of space filling is shown in Figure 11.

**Boundary Conditions—Multipass Rheometer (MPR)**

To make the problem computationally less expensive we approximate the MPR geometry by a 2-D problem in which the vorticity plane is depicted. A periodic channel is defined,
The interface is captured for \( c \) equal to 0.5. The material properties are made dependent on the local value of the concentration, \( c \), and are discontinuous across the polymer–air interface. For the air phase, \( c < 0.5 \), the fictitious-fluid properties are assigned, while for the case \( c > 0.5 \) the polymer properties are chosen. We also perform particle tracking, using Equation (47), but instead of prescribing at the inlet boundary a concentration value \( c \), we prescribe a time label, \( t \), convecting basically the flow history. The boundary conditions in the computational domain \( \Omega \), Figure 13, are specified at \( \Gamma_w \), \( \Gamma_p \), and \( \Gamma_v \), designating the mold entrance, mold walls, and the air vents, respectively. A fully developed velocity profile at the slit inlet \( \Gamma_w \) is assumed. At the mold walls we employ dynamic boundary conditions to change from slip to no-slip condition depending on the material label \( c \) at the wall. If air touches the wall, \( c = 0 \), a slip boundary condition is assigned, if instead polymer touches the wall, \( c > 0.5 \), a no-slip condition is imposed by setting a traction force at the wall. Accordingly, the boundary condition for the velocity and stress components \( u_n \) and \( \sigma_n \) in tangential direction read

\[
au_n + \sigma_n = 0 \quad \forall x \in (\Gamma_w \cup \Gamma_v),
\]

in which the dimensionless “Robin penalty parameter” \( a \) is defined as

\[
a(c) = \begin{cases} 
10^6 & \text{if } c \geq 0.5 \quad \text{no slip or leakage} \\
0 & \text{if } c < 0.5 \quad \text{slip or leakage}
\end{cases}
\]

Air is only allowed to exit the cavity at air vents, \( \Gamma_v \). For this a Robin condition is assigned for the velocity and stress components \( u_n \) and \( \sigma_n \) in normal direction,

\[
au_n + \sigma_n = 0 \quad \forall x \in \Gamma_v.
\]

As initial condition the material labels are set to zero over the entire domain \( \Omega \),

\[
c(x, t = 0) = 0, \quad x \in \Omega,
\]

and at the inlet the following boundary condition is assigned,

\[
c(x, 0 < t \leq t_{\text{inj}}) = 1, \quad \forall x \in \Gamma_w.
\]
thermal boundary conditions are specified via Dirichlet boundary conditions at the walls,

$$T = T_w \forall x \in \Gamma_w \cup \Gamma_v, \ t \geq 0.$$  \hfill (53)

**Viscoelastic Stress Problem**

As an initial condition for the MPR flow computations, the melt is in an undeformed state:

$$\mathbf{B}_e = I \quad \forall x \in \Omega, \ t = 0.$$  \hfill (54)

For both capillary and MPR computations the following boundary condition is prescribed at the inlet $\Gamma_p$ or $\Gamma_{in}$, respectively,

$$\mathbf{B}_e = I \quad \forall x \in \Gamma_{p,e}, \ t \geq 0.$$  \hfill (55)

**Computational Aspects**

We use a finite element solution algorithm to solve the flow and heat transfer problems in 3-D, developed in our group by Haagh and Van de Vosse.\[^{[68]}\] The Stokes and energy equation are coupled but solved within each time step in a segregated manner. The Stokes equations, Equation (38) and (39), that compose the flow problem are solved by a velocity-pressure formulation that is discretized by a continuous pressure of the type Crouzeix–Raviart—Galerkin finite element method (GFEM). Since the stretch of the HMW chains in the melt rises to unstable solutions with spurious node-to-node oscillations, referred to as wiggles. To overcome this problem the Streamline-Upwind Petrov–Galerkin (SUPG) method, proposed by Brooks and Hughes,\[^{[73]}\] is the most employed and thus adopted in our model.

**Stress Problem**

To perform the numerical integration of the Rolie-Poly equation, Equation (24), we use a second-order Adams–Bashford explicit scheme. For the first two time steps the numerical integration follows a first-order forward Euler method. Accordingly, the time marching scheme reads for time step $\leq 2$

$$\mathbf{B}_e^{n+1} \approx \mathbf{B}_e^n + f\left(\mathbf{u}, \mathbf{B}_e, \nabla \mathbf{u}, \left(\nabla \mathbf{u}\right)^T\right) \Delta t,$$  \hfill (56)

for time step $> 2$

$$\mathbf{B}_e^{n+1} \approx \mathbf{B}_e^n + \left(\frac{3}{2} f(\mathbf{u}, \mathbf{B}_e, \nabla \mathbf{u}, \left(\nabla \mathbf{u}\right)^T)\right)^n - \frac{1}{2} f(\mathbf{u}, \mathbf{B}_e, \nabla \mathbf{u}, \left(\nabla \mathbf{u}\right)^T)_{n-1} \Delta t.$$  \hfill (57)

Here $\mathbf{B}_e$ is the volume-invariant elastic Finger tensor.\[^{[42]}\]

**Computational Procedure: Decoupled Approach**

In our computations we adopt a decoupled approach in which the flow kinematics are assumed to be dominated by viscous forces. Every time step the rate of deformation tensor, $\mathbf{D}$, and the temperature field, $T$, are used to solve the viscoelastic Rolie-Poly equation, Equation (24), to compute the stretch of the HMW chains in the melt $A_{HMW}$ and the second invariant of the deviatoric elastic Finger (conformation) tensor of the averaged relaxation times of the melt $\mathbf{J}_2\left\{\mathbf{B}_{e_{avg}}\right\}$. The rate equations for crystallization are subsequently solved and the resulting degree of space filling is used to update the viscosity via the hardening shift factor, Equation (44). The decoupled procedure is illustrated in Figure 14 for the capillary flow problem, which requires interface tracking between the polymer melt and air. For
After an elapsed time of \( t \) becomes zero when the flow is stopped. For conditions MPR1 and MPR2, thus the time scale of the flow analysis is limited to the influence of flow conditions. Based on the crystalline morphology shown by optical micrographs, see Figure 7, one can expect the transition between the oriented shear layer and fine-grained layer to be tracked.

### Modeling Results and Discussions

#### Multipass Rheometer (MPR)

The micrographs of microtomed injection molding samples, as the ones shown in Figure 7 for the MPR experiments, denote in many cases sharp transitions between morphological layers, i.e., oriented layer, fine-grained layer, and spherulitical core. The transitions between these layers may be expected to be related to critical values of the model parameters that drive flow-induced nucleation and growth, \( \Lambda_{HMW} \) and \( J_2(\mathbf{B}_{avg}) \), respectively, and the predicted morphological parameters. Hence, we first look at the evolution of these parameters at the transition from the oriented shear layer to the fine-grained layer for flow conditions MPR1 and MPR2, whose optical micrographs clearly exhibit an oriented shear layer, see Figure 7. The time scale of the flow analysis is limited to the influence of flow on crystallization, which is determined by the relaxation of \( J_2(\mathbf{B}_{avg}) \), since the flow-induced nucleation rate \( N_f \), given by Equation (11), becomes zero when the flow is stopped. After an elapsed time of \( t = 1.5 \) s, \( J_2(\mathbf{B}_{avg}) \) becomes of \( \mathcal{O}(1) \) at the slit walls for conditions MPR1 and MPR2, thus the timescale of the flow analysis is limited to 1.5 s, after which the wall temperature is set to room temperature \( T = 23 ^\circ C \). The crystallization kinetics are calculated until the degree of space filling \( \xi_g(t) \) is 1 everywhere. To better compare all the flow conditions, we list in Table 8 the Weissenberg numbers of each condition, based on the disengagement and Rouse times of the longest molecules, with \( W_{d,R} = \dot{\gamma}_{wall} t_{d,R} \).

In Figure 15(a) we plot the time evolution of the molecular stretch (\( \Lambda_{HMW} \)) at the positions of the transition between the oriented shear layer and the fine-grained layer. Once the critical stretch, \( \Lambda_{crit} = 40 \), is reached the transition from regime I to regime II, see Figure 1, takes place, and shish start to grow at a rate, according to Equation (13), that is dependent on \( J_1(\mathbf{B}_{avg}) \), see Figure 15(c). The critical stretch is reached first for condition MPR1 at \( t \approx 0.08 \) s, which is expected based on the higher Weissenberg numbers \( W_{d,R} \) for this condition, see Table 8. The final values of the molecular stretch computed for both conditions are remarkably close to each other (for MPR1 \( \approx 90 \) and for MPR2 \( \approx 70 \)). After cessation of flow, the stretch does not relax on the time scale of the simulations, due to the coupling of the Rouse time with the number of flow-induced nuclei. The time evolution of the total number of real flow-induced nuclei \( N_{l,real} \) at the positions of the transition from the oriented shear layer to the fine-grained layer, calculated from Equation (22), is shown in Figure 15(b). \( N_{l,real} \) is found to be very similar between both conditions, just slightly lower for condition MPR2. The number density remains constant after cessation of flow due to the function \( \delta \) in Equation (11). Figure 15(d) shows the time evolution of the total real shish length per unit volume \( L_{tot,real} \), calculated from Equation (23). \( L_{tot,real} \) is found to be approximately three times higher for condition MPR1 than for condition MPR2, in agreement with the larger area underneath the curve in Figure 15(e). The values of \( \Lambda_{HMW} \), \( N_{l,real} \) and \( L_{tot,real} \) for flow conditions MPR1 and MPR2, at the transition between the oriented shear layer and the fine-grained layer are listed in Table 9. The values are of the same order of magnitude for the two flow conditions. Based on the crystalline morphology shown by the optical micrographs, see Figure 7, one can expect the transition from the spherulitical core to the fine-grained layer to be defined by a characteristic total number of flow-induced nuclei \( N_{l,fp} \). Likewise, the transition from the fine-grained layer to the oriented shear layer should be identified by the properties of the shish, either by a critical average shish length \( \langle L \rangle_{crit} \), or, more likely, a critical total

<table>
<thead>
<tr>
<th>Conditions</th>
<th>( W_{d,R} [-] )</th>
<th>( W_{d,R} [-] )</th>
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</thead>
<tbody>
<tr>
<td>MPR1</td>
<td>( 7.4 \times 10^4 )</td>
<td>( 4.4 \times 10^3 )</td>
</tr>
<tr>
<td>MPR2</td>
<td>( 6.7 \times 10^4 )</td>
<td>( 4.0 \times 10^3 )</td>
</tr>
<tr>
<td>MPR3</td>
<td>( 3.5 \times 10^4 )</td>
<td>( 2.1 \times 10^3 )</td>
</tr>
<tr>
<td>MPR4</td>
<td>( 0.8 \times 10^4 )</td>
<td>( 0.5 \times 10^3 )</td>
</tr>
</tbody>
</table>

Figure 14. Decoupled computational procedure: the kinematics of a viscous flow problem are used to solve a coupled stress-crystallization problem. The computed degree of space filling is used to update the viscosity. In the MPR case the problem is simpler, since no interface has to be tracked.
shish length per unit volume \( L_{\text{tot,crit}} \), upon which an oriented crystalline morphology becomes noticeable at a micro scale. Therefore, we postulate that within the fine-grained layer either the kinetics of flow-induced crystallization take place within regime I, see Figure 1, and, in that case, only an increase in number of spherulitical structures occurs, or the growth rate of shish is too slow or takes place within too short a period of time, so the shish stay relatively short. Regarding the shear oriented layer, we expect flow to induce only fibrillar nucleation (regime II).

We proceed comparing the model predictions in terms of \( L_{\text{tot,crit}} \), \( N_{\text{f,real}} \), and \( \langle L \rangle \) at the transitions between the different morphological layers for all flow conditions, after no further morphological changes take place. The average length of shish-kebabs \( \langle L \rangle \) can be calculated dividing the total shish length by the total number of flow-induced nuclei per unit volume:

\[
\langle L \rangle = \frac{L_{\text{tot,real}}}{N_{\text{f,real}}}
\]

In Figure 16 we plot \( L_{\text{tot,real}} \), \( N_{\text{f,real}} \), and \( \langle L \rangle \) over half of the normalized slit thickness, for flow conditions MPR1 and MPR2. The values predicted for condition MPR1 of \( L_{\text{tot,real}} \), \( N_{\text{f,real}} \), and \( \langle L \rangle \) at the transition of the shear oriented layer, are tested if they can be used as critical values that have to be surpassed for an oriented layer to become visible, see Figure 16. \( L_{\text{tot,crit}} \) denotes the critical value of \( L_{\text{tot,real}} \), \( \langle L \rangle_{\text{crit}} \), the critical average shish length, \( N_{\text{f,crit}} \), and \( N_{\text{f,fg}} \) the values of \( N_{\text{f,real}} \) found at the transition of the oriented shear layer and at the transition of the fine-grained layer to the spherulitical core, respectively. To assess the predictive capability of the model, the values \( L_{\text{tot,crit}} \), \( \langle L \rangle_{\text{crit}} \), \( N_{\text{f,crit}} \), and \( N_{\text{f,fg}} \) taken from condition MPR1, are used as morphological criteria for the other flow conditions. The value predicted for a critical shish length \( \langle L \rangle_{\text{crit}} \) is around 1 mm, which obviously is not realistic, making the comparison qualitative only and indicating that a further calibration of the model parameters is required. Typical shish lengths are thought to be in the order of microns. The computed \( L_{\text{tot,real}} \) and \( \langle L \rangle \) for condition MPR1 lie within the flow-induced crystallization region (did not cross the fine-grained layer to the spherulitical core), implying that the critical stretch \( \lambda_{\text{cri}} \) was reached only within this region. In the plots corresponding to condition MPR2 the open circles denote the critical values computed for condition MPR1. The circles fall almost on top of the curves, indicating that the different morphological criteria agree between these two conditions. However, the criterion based on total shish length \( L_{\text{tot,real}} \) seems to be in better agreement between the conditions than the one based on the average shish length \( \langle L \rangle \). The total number of flow-induced nuclei \( N_{\text{f,real}} \) at the transition between the different layers is also in good agreement between both conditions. Also for condition MPR2 the critical stretch, required for oriented crystals to grow (regime II), was reached only within the observed flow-induced crystallization region. Next, the flow conditions under which no oriented shear layer developed, namely MPR3 and MPR4, are considered. In Figure 17 we plot \( L_{\text{tot,real}} \), \( N_{\text{f,real}} \), and \( \langle L \rangle \) for conditions MPR3 and MPR4. The number of flow-induced nuclei at the transition between the fine-grained layer and spherulitical

<table>
<thead>
<tr>
<th>Conditions</th>
<th>( \lambda_{\text{HMW}} ) [-]</th>
<th>( N_{\text{f,real}} ) [-]</th>
<th>( L_{\text{tot,real}} ) m^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>MPR1</td>
<td>90</td>
<td>( 10^{12} )</td>
<td>( 0.9 \times 10^9 )</td>
</tr>
<tr>
<td>MPR2</td>
<td>70</td>
<td>( 0.77 \times 10^{12} )</td>
<td>( 0.3 \times 10^9 )</td>
</tr>
</tbody>
</table>
core predicted for conditions MPR3 and MPR4 is higher than the one predicted for condition MPR1 (open circles). The value predicted at the transition to the oriented shear layer $N_{f,\text{ori}}$ for condition MPR1 is also given as a reference at the wall, since there no oriented layer developed from conditions MPR3 and MPR4. For both conditions, however, $N_{f,\text{ori}}$ exceeds $N_{f,\text{ori}}$ from MPR1. The computed values for $L_{\text{tot,real}}$ and $\langle L \rangle$ are everywhere across the thickness smaller than $L_{\text{tot,crit}}$ and $\langle L \rangle_{\text{crit}}$, respectively, with the exception of $L_{\text{tot,real}}$ for condition MPR3 which equals $L_{\text{tot,crit}}$ at the wall. Such results are obviously important, since they imply that a critical, total or average, shish length, required for an observable oriented shear layer, was not reached. However, the computed local shish length, $L_{\text{tot,real}}$, and $\langle L \rangle$ for condition MPR3, went beyond the flow-induced crystallization region, implying that the critical stretch $L_{\text{crit}}$ was reached within the spherulitical core. This suggests that shish-kebabs might develop in the spherulitical region, however their length or volume fraction is too small.

Notice that these analyses, based on a coarse characterization done by means of optical light microscopy, can only be aimed at qualitative agreements. The definition of a critical shish length should therefore be based on a more resolved analysis based on techniques that allow to assess more detailed morphological information, such as small angle X-ray scattering (SAXS).

Oriented Volume-Based Criterion

As it was suggested in ref. [74] the relative volume of oriented crystalline material, shish-kebabs volume over the total crystalline volume, could also be used as a criterion to define the transition between the oriented shear layer and the fine-grained layer. In Figure 18(a–d) we plot the relative undisturbed volume fraction of oriented crystals, $V_{\text{ori}}$, defined as $c_0/(c_0 + f_0)$, after the completion of the crystallization process (after cooling to room temperature). The value of $V_{\text{ori}}$ computed at the transition from the oriented shear layer to the fine-grained layer in conditions MPR1 and MPR2 is almost the same ($\approx 0.026$). Again, this value seems to be rather low and further calibration of the model parameters is required. For flow conditions MPR3 and MPR4, $V_{\text{ori}}$ is everywhere across the sample thickness smaller than the critical value $V_{\text{ori,crit}}$ defined from flow condition MPR1, see Figure 18(a). This is in agreement with the experimental results that no visible oriented shear layer developed under flow conditions MPR3 and MPR4. Comparing conditions MPR1 and MPR2, the values of $V_{\text{ori}}$ computed toward the slit wall for condition MPR2 are higher. To understand this we plot in Figure 16. Distribution across half of the normalized slit thickness of the total shish length $L_{\text{tot,real}}$, the number of flow-induced nuclei per unit volume $N_{f,\text{real}}$, and the average shish length $\langle L \rangle$, after correcting for impingement, for flow conditions MPR1 and MPR2.
Figure 19(a) and (b) the time evolution of the total shish-kebab and spherulitical volume close to the wall, where the highest volume fraction of oriented crystals is computed. As expected, the volume of shish-kebabs is higher for condition MPR2. Contributing to this, is the larger computed value for $L_{\text{tot,real}}$, see Figure 16, and the radial growth of kebabs. The predicted spherulitical volume for condition MPR2 is also found to be smaller than condition MPR1, further favoring a higher volume fraction of oriented crystals. The time evolution of the radial growth rate $G(T, p)$, given by Equation (27), at the same position close to the wall after wall quenching is shown in Figure 20(a) for conditions MPR1 and MPR2. One can clearly see that the radial growth for condition MPR1, due to differences in cooling history, see Figure 20(b), is higher, explaining the larger spherulitical volume predicted for this condition.

Capillary Rheometer

For the capillary rheometer the coupling of the viscosity with the degree of space filling gave rise to a non-smooth stress field. To circumvent this numerical problem, which originated from a non-smooth viscosity distribution from the wall to the core, we did not couple the viscosity with the degree of space filling, Equation (43), with the consequence of reducing the effect of flow on crystallization. Figure 21 shows the computed total shish length per unit volume $L_{\text{tot,real}}$, the total number of flow-induced nuclei $N_{\text{f,real}}$ and the local average shish length $(L)$, across the thickness of the slit at position 2, see Figure 6, for the capillary experimental flow conditions. The corresponding micrographs are given on top of the figure.

To verify the validity of morphological criteria based on shish length within the capillary experiments, the values of $L_{\text{tot,real}}$ and $(L)$ computed from CA3 at the transition of the oriented shear layer to the spherulitical core are taken as criteria for conditions CA1 and CA2 (black dots). It can be seen that the dots fall on top of the curves, thus indicating that the model predicts at the transition of the oriented layer similar values for $L_{\text{tot,real}}$ and $(L)$, for completely different filling conditions. The open circles denote the critical values computed from condition MPR1. The values for $L_{\text{tot,real}}$ computed at the transition to the oriented layer are close to $L_{\text{tot,cr}}$ obtained from MPR1. However, the predicted values for $(L)$ for flow conditions CA1, CA2, and CA3 are 3 orders of magnitude lower than the predicted value for the MPR experiments, which is mainly
due to the higher predicted critical number of flow-induced nuclei $N_{\text{ori}}$ (2–3 orders higher). The criterion based on the total shish length per unit volume $L_{\text{tot, crit}}$ is the one that gives the best agreement between the different experimental setups. It suggests that it is the total shish length per unit volume that determines the visibility of an oriented layer, and not the actual local shish length. The non-isothermal flow conditions under which the capillary experiments take place might explain the morphological differences. Nevertheless the model seems to give consistent results within each series of experiments, i.e., the average shish length criterion is valid within the MPR and the capillary rheometer experiments, and a reasonably good agreement in terms of $L_{\text{tot, real}}$. It is also interesting that the model captures the transition layer between the skin and shear layers. For all the conditions, almost everywhere in this region the critical stretch of the long chains $L_{\text{HMW}}$, which has to be surpassed for oriented crystals to grow (regime II), was not reached. It can be seen in Figure 21 that no shish-kebabs are predicted in that region by the model. This means that the coupling between the fast cooling close to the wall, and the transient viscoelastic behavior is captured quite well.

Oriented Volume-Based Criterion

The computed volume fraction of oriented crystals at the transition to the oriented shear layer for the experimental condition MPR1 ($V_{\text{ori}} = 0.026$), was defined as a criterion $V_{\text{ori, crit}}$ to identify the transition to the oriented shear layer.

In Figure 22(a–c) we plot the volume fraction of oriented crystals for capillary conditions CA1, CA2, and CA3, respectively. The critical value $V_{\text{ori, crit}}$ taken from the condition MPR1, is plotted as an open circle. For all flow conditions the predicted volume fraction of oriented crystals at the transition to the shear layer is remarkably similar, and the values are very close to the critical value.
For conditions CA2 and CA3 the agreement is excellent; \( V_{\text{ori,crit}} \) falls on top of the computed curves. This strongly indicates that the criterion based on \( V_{\text{ori,crit}} \) holds for experiments conducted under quasi-isothermal (MPR) and non-isothermal (capillary rheometer) conditions.

Due to start-up effects, which become more noticeable at high piston speeds (short flow times), the calculated average velocity in the slit for condition CA1, see Table 6, is overestimated. This could explain the lower predicted thickness of the oriented shear layer for this condition.

Based on the excellent agreement found for conditions CA2 and CA3, we plot for these conditions in Figure 23(a) and (b) the predicted and measured thickness of the oriented region at different positions along the slit. The predicted thickness of the oriented layer is close to the measured values and

\[ \text{Figure 21. Distribution across half of the normalized slit thickness of the total shish length } L_{\text{tot,real}}, \text{ the number of flow-induced nuclei per unit volume } N_{\text{f,real}}, \text{ and the average shish length } \langle L \rangle, \text{ after correcting for impingement, for flow conditions CA1, CA2, and CA3, at slit position 2.} \]

\[ \text{Figure 22. Distribution across half of the normalized slit thickness of the relative volume of oriented material, } V_{\text{ori}} = \frac{\psi_c}{\psi_0 + \psi_c}, \text{ at slit position 2: (a) flow condition CA1, (b) flow condition CA2, and (c) flow condition CA3.} \]

\[ V_{\text{ori,crit}} \] For conditions CA2 and CA3 the agreement is excellent; \( V_{\text{ori,crit}} \) falls on top of the computed curves. This strongly indicates that the criterion based on \( V_{\text{ori,crit}} \) holds for experiments conducted under quasi-isothermal (MPR) and non-isothermal (capillary rheometer) conditions.
agrees well with the experimental trends: the thickness of the oriented crystalline region is higher at the center (position 2) of the slit.

Conclusion

In conclusion, we present in this study a model to predict the resulting morphology of semi-crystalline polymers when processed via injection molding prototype flows. A model within the framework of molecular-based rheological modeling is proposed, in which quiescent and flow-enhanced crystallization processes are coupled to the flow history, and the deformation of long chains is assumed to drive flow-enhanced nucleation. The model is tested on a set of experimental results obtained using special experimental devices in which the processing history, i.e., deformation and thermal history, is accurately controlled. The approach adopted in this study aimed at, first of all, predicting flow-induced crystallization processes coupled to the flow history, and the deformation of long chains is assumed to drive flow-enhanced nucleation. The model is tested on a set of experimental results obtained using special experimental devices in which the processing history, i.e., deformation and thermal history, is accurately controlled. The approach adopted in this study aimed at, first of all, predicting flow-enhanced crystallization processes created under quasi-isothermal conditions (MPR) and then under non-isothermal conditions (capillary rheometer) that mimic injection molding conditions. The model predictions in terms of number, size and shape of crystalline structures for both non-oriented and oriented crystals, allows to establish criteria in terms of total shish length per unit volume $L_{\text{tot,real}}$, average shish length ($L$) and volume fraction of oriented crystals $V_{\text{ori}}$, to identify the onset of an oriented shear layer. Such criteria are found to be in reasonably good agreement within the different experimental setups, between the tested flow conditions. Also, the predicted number of flow-induced nuclei at the transition of the morphological layers is found to be in agreement between all flow-conditions, within the MPR and capillary experiments. However, it is important to stress, based on the model results, that criteria defined by $(L)_{\text{ori}}$, do not hold between isothermal and non-isothermal flow conditions. In contrast, criteria based on $L_{\text{tot,real}}$ and $V_{\text{ori}}$ seem to give a quantitative agreement between all experiments, i.e., quasi- and non-isothermal flow conditions, in terms of a critical value for the transitions. We cannot make a quantitative comparison between measured and computed morphological measures due to lack of experimental data and, therefore, can also not tune our model parameters. However, the morphological information predicted by the model is essential to construct the material microstructure, which could be embedded in a multiscale modeling framework, as proposed in ref. [75] to relate morphology to properties. Such approaches employ representative volume elements (RVEs) of the microstructure to predict the macroscopic mechanical response, using the microscale information to build an engineering-scale material model.

Summarizing, we find the present results encouraging, in that a unified model for quiescent and flow-induced crystallization can be developed, sensitive to the molecular weigh of the material, with few fitting parameters and generalized to other materials.

Practical Aspects of Crystallization Modeling

The application of elaborate models to predict the morphology of semi-crystalline materials, as the one presented in this study, in commercial software is still restricted by reasons of economical and practical nature. The main difficulty originates from the extensive material characterization required. A complete rheological characterization of the material is needed to determine the spectrum of relaxation times. Additionally, the characterization of quiescent crystallization kinetics has to be done in experiments in which spherulites are counted under an optical microscope for different thermal and pressure histories. Furthermore, the approach suggested here to assess flow-induced crystallization kinetics combines the use of rheometry with numerical modeling, in which changes measured in the elastic modulus $G$ during crystallization, are predicted and used to fit the model parameters $g_n$ and $g_s$. Last but not least, saturation studies also have to be done to determine the saturation level of flow-induced crystallization, which involve a shear flow device, e.g., Linkam shear cell, and optical microscopy. Hence, as the understanding of flow-induced crystallization phenomena improves, material data are required to feed rheological and kinetic models.

From a numerical point of view, the model presented here also puts some demands on currently available.
software, as it requires two additional coupled problems to be solved: a two-mode viscoelastic stress problem, and a crystallization problem. The spatial discretization of the domain has to be sufficiently resolved to compute a smooth viscoelastic stress field and, consequently, the crystalline morphology. Using explicit integration schemes to compute viscoelastic stresses, as the one adopted here, time steps become limited by the viscoelastic stress problem. Hence, computation times are significantly increased.

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