Flow-induced crystallization of polymers
Modeling morphology and kinetics

Peter Roozemond
Flow-induced crystallization of polymers: modeling morphology and kinetics by Peter C. Roozemond

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Modeling morphology and kinetics

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Peter Cornelis Roozemond

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Dit proefschrift is goedgekeurd door de promotoren en de samenstelling van de promotiecommissie is als volgt:

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Summary

Semi-crystalline polymers, such as polyethylene (PE) and isotactic polypropylene (iPP), constitute a class of materials that combine low cost with easy processability and good properties. These materials can be easily shaped at high temperatures and their crystalline structure at temperatures below the melting point makes them useful in many applications requiring for example good mechanical or barrier properties. As these properties are a direct consequence of the crystalline microstructure, which is strongly dependent on thermo-mechanical history, it is of vital importance to have a good understanding of the influence of processing conditions on crystalline morphology. The work presented in this thesis aims to quantify flow-induced structure formation at varying temperature and pressure, as well as the crystallization kinetics of such structures.

For relatively mild flow conditions, the effect of flow is limited to an increased number of nucleation sites (leading to faster kinetics, as crystal growth rate is unaffected), while the final morphology remains predominantly isotropic. Rheometry is a well-suited experimental technique to study the effect of flow in such conditions. In this Thesis, it is shown that a suspension of soft spheres in a viscoelastic matrix is, in terms of linear viscoelastic properties, an accurate representation of a crystallizing melt. By applying a model for such systems, we can calculate the rheological properties as a function of crystalline volume fraction if the properties of the pure melt and crystallized material are known. This approach can be combined with a phenomenological model for flow-induced nucleation to describe the rheological response of poly(1-butene) during crystallization-enhancing simple shear and uniaxial extensional flow. It is shown that apparent saturation of flow-enhanced nucleation density can be explained purely from rheological considerations.

A phenomenological model that couples flow-induced nucleation rate directly from deformation on a continuum level is used throughout this Thesis. An alternative model is also proposed that departs from a reservoir of fixed size of precursors with varying size. Precursors need to overcome an energy barrier in order to nucleate. This barrier is related to their size, which can be increased through the application of flow.

For strong flow conditions, the effect of flow is no longer limited to an increase in nucleation density. Additionally, highly oriented structures are created. These structures, known as shish-kebabs, consist of a fibrous backbone with lamellar overgrowth. The critical flow conditions for the appearance of shish-kebabs has received attention from a number of authors in the literature. It is shown that the onset of shish-kebab formation in extensional flow, causing a sharp upturn in viscosity, coincides with the high-molecular weight tail entering the strain hardening regime. Experiments with the novel RheoDSC device demonstrate the rheological signature of shish-kebabs in an edge layer in plate-plate rheometry.
Rheometry can be used to measure flow-induced crystallization in homogeneous flow fields at relatively mild conditions. However, to study flow-induced crystallization at flow rates more relevant to processing conditions, we focus on a different type of experiment. The polymer melt is confined between two pistons in a slit. Simultaneously moving both pistons in the same direction, the material is subjected to a Poiseuille flow. This setup allows for the study of flow-induced crystallization at extremely high shear rates. A layer with shish-kebab morphology forms in the high shear rate region near the wall. With increasing flow strength the thickness of this “shear layer” increases. The crystallization kinetics within the slit are measured with in-situ Wide Angle X-Ray Diffraction (WAXD), while the rheology of the material is probed with a pressure drop measurement over the flow geometry. Ex-situ Polarized Optical Microscopy (POM) and Transmission Electron Microscopy (TEM) are used to determine the crystalline morphology in a qualitative sense.

Using this set-up, the crystallization kinetics of shish-kebab structures in iPP are studied. For this material an additional crystal morphology (the daughter morphology) grows epitaxially on the kebabs. The well-known Schneider rate equations are adapted to incorporate the nucleation and growth of daughters. Both morphologies (kebabs and daughters) compete for the same volume. The volume is divided between the two according to the morphologies' momentary crystal growth rates, which depend on temperature and chain conformation. The specific shish length is an adjustable parameter in this approach. Therefore this model can be used to quantify the specific shish length from the evolution of crystallinity. It is shown that for extensional flow, specific shish length can reach values more than one order of magnitude higher than in channel flow.

Finally, the crystallization kinetics within the shear layer are quantified for varying flow rate and time. Surprisingly, the flow condition has no effect on the crystallization rate, revealing a self-regulating effect of structure formation; shish affect the rheology of the melt in such a way that the viscosity is increased, locally lowering deformation rates thus arresting shish formation. Based on these findings, a model is formulated that describes formation, saturation, and crystallization of shish. The model is validated in terms of morphology, rheology, and crystallization kinetics.
Chapter 1

Introduction

1.1 Background

Semi-crystalline polymers can be easily shaped at high temperatures and their crystalline structure after cooling down gives them good mechanical and barrier properties. Because of their low cost and easy moldability resulting in fast production processes, this class of materials is widely used in a host of applications. In quiescent conditions, i.e. leaving material to cool down from the molten state without disturbing it, nucleation sites will start appearing once the temperature is below the melting point. From these nucleation sites, crystal lamellae grow radially outward forming (in most cases) spherical crystalline structures called spherulites, not unlike the ice crystals on one’s windscreen on a cold winter morning (Fig. 1.1(a)). However, if the polymer is subjected to flow during cooling, like the air around a side mirror, the final crystalline structure is no longer isotropic. Instead, crystals are oriented along flow direction, akin to the ice crystals on a side window of one’s car (Fig. 1.1(b)).

![Figure 1.1: Isotropic (a) and oriented (b) crystalline structures.](image)

The phenomenon described above, known as flow-induced crystallization (FIC), has important consequences for production processes that rely on shaping semi-crystalline polymers in their molten state, for example injection molding, blow molding, and fibre spinning. The reason is that the crystalline structure determines to a great extent mechanical, optical, and barrier properties\cite{1, 2}. An illustrative example is an injection molded product of isotactic polypropylene, which is composed of layers with a different microstructure and even different phases (Fig. 1.2). At the surface, where
the material that first enters the mold comes in contact with the cold wall, a skin layer is located consisting of quenched material. In this layer, the material is cooled through the temperature window for crystallization in such a short time that the material has no time to fully crystallize, and instead forms mesophase. Inwards towards the center of the product, we find a shear layer where flow effects dominate, resulting in highly oriented crystalline structure. Formation of this layer is one of the main topics in this thesis. Even further from the wall we find a fine-grained layer, where the effect of flow is limited to an increase in nucleation sites, the final morphology of which is still isotropic, but in which the crystallization kinetics are strongly enhanced. The crystallization in the core of the product is influenced by packing pressure, but largely unaffected by flow.

Figure 1.2: Layered crystalline structure in an injection-molded product.

1.2 State of the art

The work from the group of Janeschitz-Kriegl and co-workers can be considered as one of the milestones in the field of flow-induced crystallization of polymer melts. They introduced the short-term flow protocol to systematically study FIC[3]: a sample is subjected to a well-defined flow field for a duration short compared to the crystallization time, and isothermal crystallization is monitored afterwards. Because timescales for flow and crystallization are separated, this protocol isolates flow-induced structure formation. Using this protocol, flow-induced point-like nucleation (appearing for low to mild flow rates) has been thoroughly characterized using a shear cell combined with optical microscopy, on isotactic polypropylene (iPP) [4–9], isotactic poly(1-butene) (iPB)
Introduction

[10--12], and polylactic acid (PLA) [13]. Alternatively, a rheometer can be used to apply flow and monitor subsequent crystallization qualitatively in terms of rheology [13--19]. Using a model for the crystallinity dependence of rheological properties[20, 21], it is even possible to extract nucleation density from rheological data [9, 16]. The evolution of rheological properties with flow-induced structure formation may also play a complex role when strong flows are concerned; it has been observed that the amount of flow-induced structure saturates at a certain level, presumably due to a decreasing deformation rate caused by increasing viscosity with amount of structure[22, 23]. For high deformation rates, the effect of flow is no longer limited to an increased in nucleation sites, but oriented structures appear. The transition is quite sharp, and the critical flow conditions for the appearance of oriented structures received attention from a number of authors [3, 16, 24--28]. For such experiments a shear cell is combined with in-situ X-Ray Diffraction (XRD) [29--35], birefringence [3, 7, 24], light scattering [36], or examined ex-situ with microscopy [31]. The critical flow condition is usually expressed in terms of stress [25, 31], mechanical work [16, 26], or shear rate for a fixed strain [24]. It has been shown in a number of papers that long chains, although their concentration in such structures is not higher compared to the rest of the material [37], play a catalytic role in the formation of shish-kebabs [7, 22, 28, 30, 38].

Another issue concerns the speed at which flow-induced structures crystallize. The well-known Kolmogorov-Avrami equation [39, 40] accurately captures the crystallization kinetics spherulites, even when their number density is strongly increased by flow[16, 41]. However, when it comes to shish-kebab structures, in-situ XRD has revealed that the Avrami model often fails [30, 42--44].

Regarding the modeling of structure creation, most authors relate flow-induced crystallization to deformation on a continuum level. The Janeschitz-Kriegl group found scaling laws for the flow-induced nucleation density as a function of mechanical work [45]. Their approach was extended by the Peters group, who coupled flow-induced nucleation rate to backbone stretch[46--49]. Because the chains on the high side of the molecular weight distribution are most likely to be stretched, this effect is dominated by the longest chains in the material [5, 10, 46, 50]. Based on an extension of the Schneider rate equations [51] proposed by Eder and co-workers [3, 52], Zuidema et al. proposed a model that calculates shish density, i.e. the line nucleation density for kebabs, from continuum-level deformation [46]. Their model was validated to accurately capture the shear layer thickness in a number of experiments [46, 49]. Several other authors have adapted an expression for free energy to incorporate deformation and derive a nucleation rate from this [19, 53--59]. Ultimately, all these models are of a phenomenological nature which capture experimental data quite well, but lack predictive capabilities. Moreover, the aforementioned models based on a free energy expression calculate crystallization rate, but give no information about the final morphology. Because the final properties are governed by the crystalline morphology, we have chosen to adopt the approach pioneered by the Janeschitz-Kriegl group. Finally, some work has been performed on models on a molecular level [60--63]. Although insightful, this approach is too computationally expensive for process modeling.

1.3 Scope and outline of the thesis

The research presented in this thesis is aimed at modeling various aspects of flow-induced crystallization in polymer melts. The goal is not to develop a predictive model that can be used for the modeling of production processes. Rather, the models presented in this thesis serve to fully exploit experimental data, which are often too complex to yield quantitative results without an intermediate modeling step. However, the different models developed in this Thesis can serve as building blocks in a code for modelling production (shaping) processes.

In Chapter 2 we validate a model that couples the variation of rheological properties to space filling
of spherulites, with the help of the novel RheoDSC device. In Chapter 3 this model is combined with a phenomenological model for flow-induced nucleation to model shear and extensional flow induced crystallization in poly(1-butene). It is shown that apparent saturation of flow-enhanced nucleation density can be explained purely from rheological considerations, and that the onset of shish-kebab formation in extensional flow, causing a sharp upturn in viscosity, coincides with the high-molecular weight tail entering the strain hardening regime. A study of flow-induced crystallization in the RheoDSC device is presented in Chapter 4, which demonstrates important experimental artefacts that could occur in stand-alone rheometric studies of FIC.

Chapter 5 regards crystallization kinetics of shish-kebab structures. It is demonstrated that these can be accurately described by considering a temperature and conformation dependent growth rate. In Chapter 6 we report on crystallization kinetics within the shear layer for flows with very high wall shear rates (up to \( \approx 1000 \text{ s}^{-1} \)). Surprisingly these show no dependence on flow rate or time, revealing a self-regulating effect of structure formation due to a sharply increasing viscosity with the formation of shish. Based on these findings, we formulate a model describing formation, saturation, and crystallization of shish in Chapter 7. The model is validated in terms of morphology, rheology, and crystallization kinetics. In Chapter 8 we present a model for flow-enhanced nucleation based on the dormant precursor concept. Finally, in Chapter 9, we reiterate the main conclusions of this thesis and give our recommendations for the direction of future research in the field of flow-induced crystallization.
Chapter 2

Suspension-like hardening behavior of HDPE and time-hardening superposition

Abstract

The rheology of solidifying high-density polyethylene (HDPE) is investigated. Experiments on an HDPE were performed with a novel RheoDSC device. Results agree quantitatively with calculations for a suspension of elastic spheres in a viscoelastic matrix except for very low values of space filling (< 5%), indicating that the rheological behavior of the crystallizing melt in the frequency range investigated is purely suspension-like. The hardening behavior of the material is characterized in two different ways; a normalized rheological function and a time-hardening superposition (THS) master curve of rheological properties. An improvement is proposed to the procedure for performing THS that was previously used in the literature. Based on this procedure, a novel method for predicting the rheological properties of crystallizing melts is presented.

2.1 Introduction

Detailed knowledge of the change in rheology of semi-crystalline polymers during solidification is of vital importance for modeling of processes such as injection molding, fiber spinning, electrospinning etc, because the rheological properties, flow field and crystallization kinetics are all intimately coupled [5, 49]. A vast amount of experiments investigating the change of rheological properties can be found in the literature, cf. [64--70]. To quantify the hardening behavior of the material, commonly a normalized rheological function (NRF) is used.

\[
\Gamma(\xi) = \frac{|\eta^*(\xi)|}{|\eta^*(\xi = 0)|}
\]  

(2.1)

where \(\Gamma\) is the hardening function, \(\xi\) space filling or relative crystallinity and \(\eta^*\) the dynamic viscosity. Among the experimental data gathered, little agreement is found between studies, as shown by Lamberti [64]. This is largely because the experimental procedure commonly used to obtain the hardening curve is prone to experimental errors: rheological properties and space filling (both as a function of time) are separately measured in respectively a rheometer (usually with less precise temperature control) and a DSC apparatus. Time-viscosity and time-spacefilling data are then combined to obtain a hardening curve. A slight difference in behavior in the two experiments might result in a large error in the hardening function. For instance, Steenbakkers and Peters [20] found the experiments from Boutahar [67, 71] showed suspension-like behavior, but in order to get quantitative agreement between experiments and calculations the space filling obtained from DSC measurements had to be adjusted significantly.

An improvement on this cumbersome method was proposed by Lamberti [64]. They developed a technique that eliminates the need for obtaining space filling and rheological properties at exactly the same temperature. However, experiments were still carried out in two different devices. More recently, the group in Leuven developed a novel apparatus that combines DSC and rheometry: the RheoDSC device [72--74]. With this device rheological and thermal signals can be obtained simultaneously on the same sample and hence both types of experiments are conducted under identical conditions.

Lamberti et al. studied a novel method to describe the viscosity increase in solidifying polymers[64]. They found that, similar to a time-temperature master curve in time-temperature superposition (TTS), a time-hardening master curve can be constructed. An empirical relation for the space filling shift factor was proposed. Custódio et al implemented this method of predicting viscosity as a function of space filling in their code for the calculation of shear flow in a multi-pass rheometer[49].

A large number of analytical models for the hardening function of suspensions have been developed [75--84]. However, many of these models are not applicable to crystallizing polymer melts. Empirical models can also be found in abundance in literature [46, 65--67, 85--92], but there is little agreement between these models. Thus, there is need for a model that is able to accurately describe rheological properties of semi-crystalline polymers during solidification.

Steenbakkers and Peters [20] reviewed a number of suspension-based models and found that the generalized self consistent method (GSCM) developed by Christensen [93--95] describes accurately the rheology of crystallizing isotactic polypropylene (iPP). However, the GSCM is not applicable to the low frequency range, where gel-like behavior instead of suspension-like behavior is observed [41, 68, 96, 97]. An extension of the GSCM, including percolation [98], did not solve this problem.

The goal of this study is to investigate the applicability of the generalized self consistent method to predicting the hardening curve and space filling shift factors of a material. To this end, data from experiments in the novel RheoDSC device on high-density polyethylene (HDPE) will be used.
for validation purposes. The experimental results and time-hardening superposition of these results are presented in section 2.2. Comparison between calculations with the GSCM and the experimental results are presented in section 2.3

2.2 Experiments

A crystallizing high-density polyethylene (HDPE) was analyzed in the prototype RheoDSC device. This instrument was constructed starting from two stand-alone commercial instruments: a Q2000 Tzero\textsuperscript{TM}DSC (TA Instruments) and an AR-G2 rheometer (TA Instruments). The DSC apparatus uses the Tzero\textsuperscript{TM} technology, which is important for the correction of the thermal resistances and capacitances of the various heat flow paths in the cell caused by the modification of the calorimetric cell environment. The AR-G2 rheometer is a sensitive instrument opening the range of ultra-low torques, which is of importance as the diameter of the measurement geometry is chosen to be of comparable dimension as the DSC sensor (5 mm). For more details the reader is referred to ref. [72]. Both the rheology and thermal signals of the RheoDSC device have been validated, as reported by refs. [72--74].

Experiments were performed at 124 °C at five oscillatory frequencies. Results for the dynamic viscosity, modulus and phase angle are presented in Fig. 2.1. Different symbols indicate the increasing space filling. The experiments show a large difference in rheology between the experiments with zero and just six percent relative crystallinity, much larger than what would be caused by a suspension of spherulites with this amount of space filling. The effect is accounted for by extrapolating the data for the crystallizing melt to obtain adjusted values for the rheology of the melt, as will be explained in the “Early stage of crystallization” section. The modulus for the fully crystallized material (\(\xi = 1\)) is also obtained by extrapolation. Values are shown in Table 2.1.
Figure 2.1: Measurements of the magnitude of the dynamic viscosity (a), phase angle (b), storage modulus (c) and loss modulus (d).

Table 2.1: Storage and loss moduli for the melt, $G'_0$, and for the fully crystallized material, $G'_1$.

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<td>2.29</td>
<td>0.062</td>
<td>0.692</td>
</tr>
<tr>
<td>3.16</td>
<td>0.142</td>
<td>2.78</td>
<td>0.087</td>
<td>0.757</td>
</tr>
<tr>
<td>10.0</td>
<td>0.223</td>
<td>3.36</td>
<td>0.121</td>
<td>0.786</td>
</tr>
<tr>
<td>31.6</td>
<td>0.324</td>
<td>3.90</td>
<td>0.132</td>
<td>0.760</td>
</tr>
<tr>
<td>100</td>
<td>0.432</td>
<td>4.42</td>
<td>0.148</td>
<td>0.734</td>
</tr>
</tbody>
</table>
2.2.1 Hardening function

Figure 2.2 shows the hardening function, calculated using a normalized rheological function (NRF) based on the magnitude of the dynamic viscosity versus space filling for the five frequencies investigated. The NRF is given by

$$\Gamma(\xi, \omega) = \frac{|\eta^*(\xi, \omega)|}{|\eta^*(\xi = 0, \omega)|}.$$  \hspace{1cm} (2.2)

The hardening curve is similar in shape to what was observed in the literature \cite{64, 74}, taking larger values for lower frequencies throughout the range of space filling. It is emphasized that in accordance with refs. \cite{64, 74}, little change in rheology is observed for space filling below 10%, whereas other authors have reported order of magnitude changes for $\xi < 10\%$ \cite{66, 70}.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure22.png}
\caption{Hardening curves calculated using Eq. 2.2 for five frequencies}
\end{figure}

2.2.2 Time-hardening superposition (THS)

Lamberti et al. found that in a frequency-viscosity plot, measurements for crystallizing iPP with different space fillings can be shifted to a single master curve, analogous to a time-temperature superposition (TTS) master curve\cite{64}. This was done by shifting the relaxation times of the material with $a_\xi$, so that the shifted frequency and viscosity become

$$\omega_{\text{master}} = \omega * a_\xi(\xi)$$
$$\eta_{\text{master}} = \eta / a_\xi(\xi)$$  \hspace{1cm} (2.3)

Lamberti et al. also found that the shift factor $a_\xi$ was reasonably well described by the empirical relation

$$\log_{10} a_\xi = \alpha_1 \xi^{\alpha_2}$$  \hspace{1cm} (2.5)

where $\alpha_1$ and $\alpha_2$ are fitting parameters.

Viscosity data from the present experiments were shifted in the same way. The resulting master curve is shown in Fig. 2.3(a). The curve for $\xi = 0$ corresponds to the values given in Table 2.1. Fig. 2.3(b) depicts shift factor versus space filling. The empirical relation from Lamberti et al. is depicted with the solid line. We observe that Lamberti's empirical relation is able to capture our data quite well.
Suspension-like hardening behavior of HDPE

Figure 2.3: Master curve of $|\eta^*|$ shifted on the viscosity (a) and corresponding shift factors (b). The solid line shows a fit with the empirical relation from Lamberti et al. with parameters $\alpha_1 = 5.19$ and $\alpha_2 = 1.20$. 

with parameters $\alpha_1 = 5.19$, $\alpha_2 = 1.20$. Lamberti studied two grades of iPP and found $\alpha_1 = 3.875$, $\alpha_2 = 1.236$ for one of the grades and $\alpha_1 = 12.073$, $\alpha_2 = 3.166$ for the other.

Actually, the procedure that Lamberti et al. used to obtain a master curve differs from the way in which TTS is conventionally conducted. In TTS the shift factor for the relaxation times of the material $a_\xi$ is obtained by shifting the phase angle and subsequently the master curve for the viscosity would be obtained by applying the shift factor for relaxation times, and an additional vertical shift factor $b_\xi$:

$$\eta_{master} = b_\xi(\xi) * \eta/a_\xi(\xi)$$  \hspace{1cm} (2.6)

If the vertical shift factor $b_\xi$ is of order 1, which is usually the case in TTS, the difference between the one step procedure that Lamberti et al. used and the conventional two step shifting procedure is small. However, if we apply Lamberti’s procedure, i.e. obtaining $a_\xi$ through shifting the dynamic viscosity, to our measurements, we observe that the phase angle curves shifted with this $a_\xi$ do not form a single master curve. This is shown in Fig. 2.4. This means that although this procedure could be used to calculate viscosity as a function of space filling, $a_\xi$ does not shift the relaxation times of the material. Therefore, the viscosity master curve constructed in this way, with its promising range of eight decades, has no physical meaning. Consequently, this master curve can not be used to obtain the dynamic viscosity of the pure melt at very high frequency by measuring the dynamic viscosity of the partly crystallized material at a lower frequency.

For this reason, we propose to use the two step procedure commonly used in TTS. The result of this procedure is presented in Fig. 2.5. Contrary to the one step procedure, this yields a smooth master curve for the phase angle, indicating that the shift factor $a_\xi$ obtained in this way is the correct shift factor for the relaxation times of the material. Compare figures 2.4 and 2.5(a). For the dynamic viscosity we also obtain a smooth master curve. Again the measurements with $\xi = 0$ correspond to the values in Table 2.1. Unfortunately, the frequency range that the master curves span is reduced to four decades. The shift factors that were used to construct these master curves are given in Figure 2.6 and Table 2.2. Although the fitting procedure is different, the empirical fit by Lamberti et al. is still
Figure 2.4: Master curve for the experimental data for the phase angle with shift factors obtained from the one step shifting procedure.

able to describe the data for the timescale shift factor. The values for vertical shift factor $b_\xi$ can be described by

$$\log_{10} b_\xi = \beta_1 \xi^2 - \beta_2 \xi.$$  \hspace{1cm} (2.7)

We observe that the phase angle measurements for the lowest frequency ($\omega = 1 \text{ rad/s}$) slightly deviate from the master curve, see Fig. 2.5(a). This indicates that THS might not give a good representation at lower oscillatory frequencies. We come back to this, and to our interpretation of the meaning of the parameters $a_\xi$ and $b_\xi$, in "Time-hardening superposition with the GSCM" section.

Figure 2.5: Master curves for the experimental data for phase angle (a) and magnitude of the dynamic viscosity (b). Data shifted using the two step procedure.
2.3 The Generalized Self Consistent Method

The crystallizing melt is modeled as a suspension of spherical soft particles (the spherulites) in a viscoelastic matrix (the amorphous melt). The properties of such a system can be calculated using the three dimensional Generalized Self-Consistent Method (GSCM), which was developed to describe the rheological properties of a suspension of spherical soft particles in an elastic medium. The basic problem of the 3D GSCM is shown in Fig. 2.7. The suspension is represented by a unit cell consisting of a particle with properties of the dispersed phase and a surrounding matrix shell with properties of the matrix phase. Their radii are $a$ and $b$, respectively. The volume fraction of the particles is given by

$$\xi = \left(\frac{a}{b}\right)^3.$$  (2.8)
The unit cell is suspended in an infinitely extending medium, which has the (unknown) effective properties of the suspension. The solution of the three phase problem yields the effective properties of the composite medium of an isotropic matrix phase into which is embedded the isotropic inclusion phase. The result for the effective medium problem of Fig. 2.7 is given by the solution of the quadratic equation \cite{93, 94}

$$Af_G^2 + Bf_G + C = 0$$

(2.9)

where \(f_G\) is the relative modulus,

$$f_G = \frac{G}{G_0}$$

(2.10)

with \(G\) the modulus of the suspension and \(G_0\) the modulus of the matrix. The coefficients \(A, B\) and \(C\) depend on space filling \(\xi\), the Poisson's ratios of the matrix and dispersed phase, \(\nu_0\) and \(\nu_1\), respectively, and the ratio between the moduli of the dispersed phase and the matrix, \(\mu = G_1/G_0\). Expressions for the coefficients \(A, B\) and \(C\) are given in the appendix. Steenbakkers and Peters\cite{20} applied the GSCM, derived for elastic materials, to viscoelastic materials by utilizing the correspondence principle \cite{99--101}. In that case, the relative modulus is complex;

$$f_G^*(\omega) = \frac{G_1^*(\omega)}{G_0^*(\omega)}$$

(2.11)

and so is the modulus ratio \(\mu^* = G_1^*/G_0^*\). The relative modulus can be calculated from

$$A^*f_G^*2 + B^*f_G^* + C^* = 0$$

(2.12)

where the complex coefficients \(A^*, B^*\) and \(C^*\) follow from \(A, B\) and \(C\) when \(\mu\) is replaced by \(\mu^*\). The absolute value of the complex relative modulus, \(|f_G^*|\), is equal to the NRF as defined in equation 2.2.

The 3D GSCM was developed for systems with purely spherical dispersed particles. Growing spherulites will impinge at some point and as a result the dispersed particles in this system will not be
purely spherical at high volume fractions (above ~70 %). Previous studies do show a discrepancy between the GSCM and rheology experiments at very high volume fractions (~98%) [16, 20]. However, below this value there seems to be no noticeable effect of impingement on the hardening behavior. In this study we examine only quiescent crystallization, with crystalline structures that are spherical (before impingement). Flow-induced crystallization may yield oriented cylindrical crystalline structures. Steenbakkers and Peters found that these have qualitatively similar hardening behavior but were not able to quantitatively capture the behavior using a 2D suspension model[20]. More research on this will be done in future work.

2.4 Results

2.4.1 Early stage of crystallization

We observe that the change in material properties from 0% to 6% space filling is much larger than would be expected from a suspension. This is illustrated in Fig. 2.8, where measurements and calculations are compared for the storage and loss moduli versus space filling for \( \omega = 1 \text{ rad/s} \). Figure 2.8(a) shows calculations where we have taken the modulus of the pure melt \( G^*_0 \) as the measured modulus of the material with no space filling. The calculations consistently underpredict the measured moduli. The discrepancy can be resolved by extrapolating \( G^*_0 \) from the data for the crystallizing melt. This was done for the calculations presented in Fig. 2.8(b), resulting in quantitative agreement for the full range of space filling.

![Figure 2.8](image-url)

Figure 2.8: Comparison of the storage modulus (open symbols: measurements, solid line: calculations with suspension model) and loss modulus (closed symbols: measurements, dashed line: calculations with suspension model) versus space filling at \( \omega = 1 \text{ rad/s} \). (a) results with \( G^*_0 \) as the measured modulus of the material with no space filling, (b) with \( G^*_0 \) extrapolated from data for the crystallizing melt (shown in Table 2.1).
Possibly, this indicates that between 0% and 6% space filling a process has taken place that has altered the melt in a way that can not be described by suspension-like behavior. Something similar is observed in the data from Carrot et al. [14], who show the evolution of storage and loss modulus for a crystallizing HDPE melt under isothermal conditions at different temperatures. A strong and very steep increase in modulus is seen soon after the onset of crystallization (\(\sim 200\) seconds). After this, the modulus increases gradually until crystallization is complete (\(10^3 - 10^4\) seconds, depending on the temperature). Carrot did not comment on the phenomenon. Perhaps a network of physical crosslinks is formed [46, 67, 71, 97, 102, 103]. Subsequently, spherulites grow in this altered melt, the effect of which is well described by suspension-like behavior. What exactly happens during the early stages of crystallization remains a lively research topic.

Furthermore, it takes the RheoDSC some time to reach thermal equilibrium, in the order of 5 minutes [104]. This is corrected for by subtracting a baseline. There is some ambiguity in the baseline, which might lead to slight inaccuracies in the space filling at short times.

For now we deal with the phenomenon by adjusting the values for the moduli of the melt as described above. Results that are presented in this study are obtained with the adjusted value for the rheology of the melt.

### 2.4.2 Validation with experimental results

Figure 2.9 shows the experimental quantities depicted in Fig. 2.1 and the results for calculations with the GSCM for the same conditions. Quantitative agreements are observed for the storage and loss modulus and for the magnitude of the dynamic viscosity (for \(\xi \neq 0\), as explained above). For \(0.063 < \xi < 0.64\) the GSCM is less accurate in predicting the phase angle, however agreement is still qualitative.
2.4.3 Hardening function

Figure 2.10 shows the hardening curve for the material, both from experiments and calculations. We observe quantitative agreement, the hardening function of this material is very well described by suspension-like behavior.

2.4.4 Comparison with scaling laws

Other authors have used scaling laws to relate the storage modulus to space filling. These scaling laws are compared to the experimental data and the GSCM in Fig. 2.11. The dash-dotted line depicts a linear scaling law[90, 105],

\[
\frac{G'(\xi) - G'(\xi = 0)}{G''(\xi = 1) - G''(\xi = 0)} = \xi. \tag{2.13}
\]
This relation performs quite poorly; storage modulus is overpredicted regardless of space filling. Instead, Pogodina et al used a logarithmic scaling law\cite{41}, the dashed line in Fig. 2.11,

\[
\frac{G'(\xi)}{G'(\xi = 0)} = \frac{G'(\xi = 1)\xi}{G'(\xi = 0)}. \tag{2.14}
\]

This relation is observed to capture the data very well. It must be noted however that this method gives no information about the loss modulus and phase angle.

2.4.5 Time-hardening superposition with the GSCM

The master curves for phase angle and viscosity obtained using the two step procedure are shown in Fig. 2.12. The corresponding shift factors are given in Fig. 2.13 and Table 2.2. We observe a good agreement; the 3D GSCM model can be used to calculate \(a_\xi\) as well as \(b_\xi\).
We observe that for the lowest frequency measurements and calculations slightly deviate from the phase angle master curve. Because this is observed both for measurements and calculations we can not attribute this to gel-like behavior, as the calculations capture only suspension-like behavior. This means that for lower frequencies, THS might be less accurate.

Figure 2.12: Master curves of the phase angle (a) and the viscosity (b). Open symbols show measurements, closed symbols show calculations. Data shifted using the two step procedure.

Figure 2.13: Shift factor $a_\xi$, open symbols are values to shift the measurements, closed symbols are the shift factors from the master curve from calculations, line is the empirical fit from Lamberti et al. with parameters $\alpha_1 = 2.08$, $\alpha_2 = 2.56$ (a). Vertical shift factor $b_\xi$, open symbols are values to shift the measurements, closed symbols are the shift factors from the master curve from calculations, line shows a fit of the form $\log_{10}(b_\xi) = \beta_1 \xi^2 - \beta_2 \xi$ with $\beta_1 = 0.22$, $\beta_2 = 1.01$ (b).
In their review of the applicability of suspension models to polymer crystallization, Steenbakkers and Peters proposed a phenomenological model for hardening behavior[20]. Suppose a relaxation spectrum \((G_i, \lambda_i)\) with \(M\) modes is known for the melt so that storage and loss modulus as a function of frequency are given by

\[
G'(\omega) = \sum_{i} G_{0,i} \frac{\lambda_{0,i}^2 \omega^2}{1 + \lambda_{0,i}^2 \omega^2},
\]

\[
G''(\omega) = \sum_{i} G_{0,i} \frac{\lambda_{0,i} \omega}{1 + \lambda_{0,i}^2 \omega^2}.
\]

(2.15) (2.16)

Now, if the number of modes is the same for both the liquid and solid phase, the moduli and relaxation times of the solid phase can be expressed in terms of the moduli and relaxation times of the matrix as

\[
G_i(\xi) = k_{G,i}(\xi) G_{0,i},
\]

\[
\lambda_i(\xi) = k_{\lambda,i}(\xi) \lambda_{0,i}.
\]

(2.17) (2.18)

with \(1 \leq k_{G,i} \leq G_{1,i}/G_{0,i}\) and \(1 \leq \lambda_{G,i} \leq \lambda_{1,i}/\lambda_{0,i}\). Storage and loss moduli as a function of frequency and space filling can then be expressed as

\[
G'(\omega, \xi) = \sum_{i} k_{G,i}(\xi) G_{0,i} \frac{\lambda_{0,i}^2 \omega^2}{1 + \lambda_{0,i}^2 \omega^2},
\]

\[
G''(\omega, \xi) = \sum_{i} k_{G,i}(\xi) G_{0,i} \frac{\lambda_{0,i} \omega}{1 + \lambda_{0,i}^2 \omega^2}.
\]

(2.19) (2.20)

Steenbakkers and Peters did not derive expressions for \(k_G\) and \(k_\lambda\). The results obtained here, i.e. the fact that a time-hardening master curve can be constructed, imply that for both \(k_\lambda\) and \(k_G\), a single value suffices for all modes, and that the storage and loss moduli as a function of space filling can be calculated using

\[
G'(\omega, \xi) = k_G(\xi) \sum_{i} G_{0,i} \frac{\lambda_{0,i}^2 \omega^2}{1 + \lambda_{0,i}^2 \omega^2},
\]

\[
G''(\omega, \xi) = k_G(\xi) \sum_{i} G_{0,i} \frac{\lambda_{0,i} \omega}{1 + \lambda_{0,i}^2 \omega^2}.
\]

(2.21) (2.22)

with \(k_\lambda = a_\xi\) and \(k_G = 1/b_\xi\).

In this study we have presented two ways to calculate the rheological properties of a crystallizing material as a function of space filling and oscillatory frequency. Figure 2.14 schematically shows both, for purpose of clarity. Time-hardening superposition is presented in Fig. 2.14(a); the two shift factors \(k_\lambda\) and \(k_G\) are independent of frequency and shift the whole \(G^*(\omega)\) curve at once. Figure 2.14(b) depicts calculation of the storage modulus via a relative modulus \(f_G^*\) which is calculated for each \(\xi\) and \(\omega\) using the GSCM.
2.5 Conclusions

The evolution of the rheology of an HDPE during solidification was analyzed. Quantitative agreement with a suspension-based model, the 3D Generalized Self-Consistent Method, was found. This indicates that in the frequency range investigated, a suspension with spherical soft particles in a viscoelastic matrix is a good representation of an amorphous melt with growing spherulites. In the early stages of crystallization a phenomenon is observed that cannot be explained by suspension-like behavior. This was dealt with by using adjusted values for the dynamic modulus of the melt.

Time-hardening superposition (THS) was performed. An improvement on the procedure developed in literature is proposed. The fact that a THS master curve can be constructed means that with a known Maxwell spectrum of the melt, the properties of a crystallizing melt can be obtained using two shift parameters that are mode and frequency independent and which can be easily measured or obtained from a suspension-based model.
2.A Coefficients in the GSCM

Expressions for the coefficients $A$, $B$, and $C$ in the 3D generalized self consistent model derived by Christensen et al. [93--95] are shown in Table 2.3.

Table 2.3: Expressions for the coefficients in the 3D GSCM

<table>
<thead>
<tr>
<th></th>
<th>for A:</th>
<th>for B:</th>
<th>for C:</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>$e_1 (\mu - 1) \eta_1 \xi^{(10/3)} + e_2 [63 (\mu - 1) \eta_2 + 2\eta_1 \eta_3] \xi^{(7/3)} + e_3 (\mu - 1) \eta_2 \xi + e_5 \eta_1 \eta_3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$B$</td>
<td>$c_1 (4 - 5\nu_0)$</td>
<td>$-4(1 - 5\nu_0)$</td>
<td>$-4(1 - 5\nu_0)$</td>
</tr>
<tr>
<td>$C$</td>
<td>$c_2 - 2$</td>
<td>$-504$</td>
<td>$252$</td>
</tr>
<tr>
<td></td>
<td>$c_3 252$</td>
<td>$-4(1 - 5\nu_0)$</td>
<td>$-4(1 - 5\nu_0)$</td>
</tr>
<tr>
<td></td>
<td>$c_4 -50(7 - 12\nu_0 + 8\nu_0^2)$</td>
<td>$150(3 - \nu_0)\nu_0$</td>
<td>$-25(7 - \nu_0^2)$</td>
</tr>
<tr>
<td></td>
<td>$c_5 4(7 - 10\nu_0)$</td>
<td>$3(7 - 15\nu_0)$</td>
<td>$-(7 + 5\nu_0)$</td>
</tr>
</tbody>
</table>

with $\eta_1 = (\mu - 1)(7 - 10\nu_0)(7 + 5\nu_0) + 105(\nu_1 - \nu_0)$

$\eta_2 = (\mu - 1)(7 + 5\nu_1) + 35(1 - \nu_1)$

$\eta_3 = (\mu - 1)(8 - 10\nu_0) + 15(1 - \nu_0)$

2.B Poisson’s ratios

To solve Eq. 2.12, the Poisson’s ratios of the continuous and dispersed phase are required. They can be calculated using the well known formula [106]

$$\nu = \frac{3K - 2G}{2(3K + G)},$$  \hspace{1cm} (2.23)

where $K$ is the bulk modulus and $G$ is the shear modulus. The bulk modulus of HDPE $K \approx 1.5$ GPa [107]. With the plateau for the storage modulus at approximately 0.4 MPa for $\xi = 0$ and at approximately 6 MPa for $\xi \approx 1$ (see Fig. 2.1) we find estimates of $\nu_0 = 0.4999$, $\nu_1 = 0.4980$. 
Chapter 3

Flow-enhanced nucleation of poly(1-butene): model application to short-term and continuous shear and extensional flow

Abstract

A modeling framework for flow-enhanced nucleation of polymers is applied to a broad set of data from literature. Creation of flow-induced point-like nuclei is coupled to chain stretch of the high-molecular weight tail of the material, calculated with a rheological constitutive model. As the flow-induced nuclei grow, the crystalline volume fraction increases, and with it the viscosity of the material. This is accounted for by describing the material as a suspension of spheres in a viscoelastic matrix. Calculations are compared with a broad set of experimental data from literature on three grades of poly(1-butene). First, a parameter set is determined by fitting model results to flow-induced nucleation densities from short-term shear experiments. Next, this parameter set is used to validate the framework in continuous flow experiments, in which viscosity is monitored during a constant flow rate. In this way we demonstrate the approach is applicable to not only short-term shear, but also continuous flow. It was observed in experiments that, for continuous extensional flow, the viscosity shows an upturn at a constant strain, the value of which is independent of strain rate. We hypothesize that this upturn is related to long chains entering the chain stretch regime, as a result of the extension rate exceeding the inverse of the Rouse time of the longest chains.

3.1 Introduction

The mechanical and optical properties of semi-crystalline polymer products strongly depend on crystalline structure \([1, 108--110]\), which is largely determined by processing conditions \([4, 111]\). The development of a quantitative model for flow-induced crystalline structure formation is therefore a vital step towards predicting properties of polymer products.

The majority of experimental work on flow-induced crystallization (FIC) has followed the short-term shear protocol proposed by the group of Janeschitz-Kriegel \([3]\), which was spawned by the idea that if the crystallization time is much longer than flow time, it can be assumed that the only effect of flow is creation of structure; crystalline growth rate is unaffected. Because of the short flow times, this method is suitable for investigating FIC up to flow rates that are relevant for industrial processing conditions. Important findings include the dominant role of the high-molecular weight tail in creating nucleation sites \([15, 26, 37, 112, 113]\) and the importance of various rheological timescales in the material \([111]\).

Alternatively, FIC can be investigated in a continuous flow experiment. In these types of experiments the material is subjected to a constant flow rate in a rheometer and the viscosity is monitored. At a certain point in time the viscosity will show an upturn due to crystallization. The time at which this happens is a measure for the crystallization-enhancing effect of flow. These types of experiments have been performed in rotational flow \([17, 19]\) as well as extensional flow \([18, 114, 115]\). Flow times are typically higher than for short-term flow experiments, which at high shear rates might result in destruction of the sample. Therefore this approach is mainly suited for low shear or extension rates.

The derivation of a predictive model for FIC has been attempted in a number of ways. Some researchers started with the classical result for homogeneous nucleation known as the Hoffman/Lauritzen expression,\([19, 53]\) which contains the free energy as a driving force. The entropic part is adapted by including the decrease due to the molecular orientation caused by the flow. A model using this approach was derived by Ziaibiki and Alfonso, but the entropy change due to orientation alone could not reproduce effects as dramatic as observed in experiments \([55]\). A second approach starts from the statistical description of the evolution of the precursor size distribution in the melt \([54]\) and, again, incorporates the effect of flow by adapting the free energy. On the level of the precursors, a Monte-Carlo approach was used by Graham and co-workers \([61, 62]\), leading to insight into the relation between segmental orientation and the nucleation process and providing support for modeling on a continuum level, although this approach is not useful on the level of process modeling due to computational expensiveness. Based on experimental observations, Eder and Janeschitz-Kriegl proposed a set of differential equations \([7, 52]\) analogous to the Schneider rate equations \([51]\) for point nucleation and subsequent spherulitical growth, that captured the observed correlations between measures for crystalline structure (i.e. number and size of fibrils) and the applied flow. Shear rate was used as the driving force for flow-enhanced nucleation and subsequent fibrillar growth.

Taking this set of equations, Zuidema et al. \([46]\) replaced the shear rate with the second invariant of the deviatoric part of the stress in the high molecular weight tail, a measure that combines the molecular orientation and stretch. This phenomenological approach successfully captured the vast amount of experimental observations on isotactic polypropylene (iPP) from the group of Eder and Janeschitz-Kriegl. The nucleation model was studied and validated further by Custódio \([49]\) and Steenbakkers \([5]\). Applied to iPP, the model captures short-term shear experimental results very well, in simple shear \([5, 116, 117]\) as well as in channel flow \([46, 49]\). Steenbakkers \([118]\) applied the model to data on poly(1-butene) from the group in Leuven, who studied this material extensively \([24, 119]\). Roozemond et al. \([116]\) showed that a similar model derived from the concept of flow-activatable
dormant precursors [4, 45] yields qualitatively comparable results.

In this work we study the predictive capability in continuous flow of the nucleation model first developed by Zuidema. To this end, we compare calculations with experimental data from various sources on three grades of isotactic poly(1-butene) (iP1B) of which the rheology was well-characterized. Parameters for the nucleation model are first determined from fitting to short-term shear experiments [120]. Then, using the same parameters, the model is validated in continuous simple shear and uniaxial extension flow [17--19]. The Schneider rate equations [51] and a suspension model [20, 21], are used to calculate crystalline volume fraction and resulting viscosity increase in time. The goal of this paper is not to improve or adapt the existing model, but rather to investigate how well the experimental data presented here could be captured by the model and, if required, could be used for model improvement in future work.

In section 3.2 we give some material characteristics and information about the experiments. The modeling framework is presented in section 3.3. Experimental results and calculations are compared in section 3.4. The conclusions from this work are summarized in section 3.5.

### 3.2 Experimental

#### 3.2.1 Materials

Three commercial grades of isotactic poly(1-butene), produced by LyondellBasell, were used in the experiments to which calculations are compared in this study. Information about the molecular weight distributions are given in table 3.2. A multi-mode Maxwell spectrum was fitted to rheological data from literature, see Fig. 3.1(a) and table 3.1. The reptation time of the slowest Maxwell mode, corresponding to the inverse of the oscillatory frequency at the onset of the terminal regime, was taken as the relaxation time representing the high molecular weight tail for our nucleation model. The corresponding Rouse time was calculated using [121]

$$\lambda_R = \frac{\lambda_{rep}}{3Z}$$

where $Z$ is the number of entanglements per chain as in table 3.2. The molecular weight between entanglements was taken as $M_e = 18$ kg/mol [24]. The Rouse times of the longest modes, which are used to calculated stretch for input in the nucleation model, are given for all materials at 100 °C in table 3.3.

<table>
<thead>
<tr>
<th>Material</th>
<th>$\lambda_k$ [s]</th>
<th>$G_k \cdot 10^3$ [Pa]</th>
<th>$\lambda_k$ [s]</th>
<th>$G_k \cdot 10^3$ [Pa]</th>
<th>$\lambda_k$ [s]</th>
<th>$G_k \cdot 10^3$ [Pa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PB800</td>
<td>0.0018</td>
<td>25.5</td>
<td>0.0036</td>
<td>52.9</td>
<td>0.0027</td>
<td>54.6</td>
</tr>
<tr>
<td>PB400</td>
<td>0.018</td>
<td>0.64</td>
<td>0.029</td>
<td>10.6</td>
<td>0.024</td>
<td>34.3</td>
</tr>
<tr>
<td>BR200</td>
<td>0.25</td>
<td>0.0020</td>
<td>0.15</td>
<td>1.53</td>
<td>0.16</td>
<td>22.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.89</td>
<td>0.040</td>
<td>1.4</td>
<td>11.4</td>
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<td></td>
<td></td>
<td></td>
<td>0.10</td>
</tr>
</tbody>
</table>
Flow-enhanced nucleation of P1B

Figure 3.1: (a) Storage and loss moduli of the three grades at a reference temperature of 180 °C. Open symbols show measured storage modulus, closed symbols show measured loss modulus. Solid and dashed lines give storage and loss moduli from the Maxwell spectrums given in table 3.1. Data for PB800 and PB400 from ref. [12], data for BR200 from ref. [17]. (b) Crystal growth rate of the three grades as a function of temperature, from ref. [122].

It is well known that P1B can crystallize in a number of polymorphs, cf. ref. [123]. Crystals from the melt form in the kinetically favorable phase II, which after solidification transform to the stable phase I. This transformation is relatively slow and does not take place during the experiments with conditions as discussed here [24]. All crystallites in these conditions form in phase II and the transformation to form I is outside the scope of this work.

To calculate space filling during continuous shear using the Schneider rate equations, the crystal growth rate is used. Data for all three grades are presented in Fig. 3.1(b).

Table 3.2: Molecular and rheological properties (\(M_n\) is number average molecular weight, \(M_w\) is weight average molecular weight, \(M_e\) is molecular weight between entanglements, \(E_a\) is flow activation energy, \(T_m^0\) is thermodynamic melting point [17, 119, 122, 124])

<table>
<thead>
<tr>
<th></th>
<th>PB800</th>
<th>PB400</th>
<th>BR200</th>
</tr>
</thead>
<tbody>
<tr>
<td>(M_w) [kg/mol]</td>
<td>85</td>
<td>176</td>
<td>762</td>
</tr>
<tr>
<td>(M_w/M_n)</td>
<td>5.1</td>
<td>5.7</td>
<td>19.6</td>
</tr>
<tr>
<td>(Z = M_w/M_e)</td>
<td>4.7</td>
<td>9.8</td>
<td>42</td>
</tr>
<tr>
<td>isotacticity [mmmm]</td>
<td>79.5</td>
<td>79.5</td>
<td>89.9</td>
</tr>
<tr>
<td>(E_a) [kJ/mol]</td>
<td>41.0</td>
<td>47.2</td>
<td>54.7</td>
</tr>
<tr>
<td>(T_m^0) [°C]</td>
<td>130.4</td>
<td>134.0</td>
<td>138.1</td>
</tr>
</tbody>
</table>

Table 3.3: Rouse times of the high molecular weight tail of the materials at 100 °C.

<table>
<thead>
<tr>
<th></th>
<th>PB800</th>
<th>PB400</th>
<th>BR200</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\lambda_{R,hmw}) [s]</td>
<td>0.18</td>
<td>0.44</td>
<td>22.5</td>
</tr>
</tbody>
</table>
3.2.2 Short-term shear flow experiments

Short-term shear experiments were performed at the University of Genova on grades PB800 and BR200 in a Linkam CSS 450 rotational shearing device [120, 125]. Thermo-mechanical history was erased at 180 °C before cooling down to a temperature where a shear pulse was applied. The shear rate, shear time and shear temperature were varied. For PB800 the shear temperature $T_{\text{shear}}$ was varied between 83 °C and 97 °C, for BR200 $T_{\text{shear}} \in (100, 160)$. After shear, the material was monitored using optical microscopy. The number of nuclei in the observation window was counted from which nucleation density was estimated. PB800 was held at the shear temperature to crystallize, the BR200 samples were cooled down to 96 °C because of the low growth rate at the shear temperatures. These experimental results were used to determine the parameters in the nucleation model.

3.2.3 Continuous flow experiments

Calculations are compared with results from continuous flow experiments from various sources [17--19]. In these types of experiments, the polymer melt is subjected to a constant shear or extension rate in a rheometer while the viscosity is monitored. For shear, a plate-plate set-up is used. Uniaxial extensional flow experiments were done using an extensional viscosity fixture (EVF), which was introduced by Sentmanat [126]. We will compare predictions from the model and experimental data for the transient viscosity signal for rotational and extensional rheometry. Hadinata et al. [17] showed, using ex-situ optical microscopy, that for the shear experiments all crystallites were isotropic spherulites. Therefore the assumption that only isotropic structures are formed holds for the shear experiments. The experiments with extensional flow might yield oriented structures, we come back to this in the "Results" section.

3.3 Theory

3.3.1 Nucleation model

The aim of the present work is to demonstrate the applicability of this approach to short-term shear as well as continuous flow. To this end, the full model formulation as first developed by Zuidema et al. [46] and improved by Steenbakkers and Peters[5] was simplified in some aspects. In the range of flow conditions of interest in this work the effect of these simplifications is minor and the number of fitting parameters is reduced considerably. In this section we present only the governing equations of the simplified model, the simplifications with respect to the full model are discussed in Appendix A.

The polymer chains orient and stretch as the material is subjected to deformation. Regions with highly stretched molecules can act as nucleation sites. In a polydisperse melt, this effect is most pronounced for the high molecular weight (hmw) chains of the material, as these are more susceptible to deformation than shorter chains. The creation rate of flow-induced nuclei is coupled to the stretch in the high-molecular weight tail of the material. This is expressed as

$$\frac{dN_{nf}}{dt} = g_n \left( \Lambda_{\text{hmw}}^4(t) - 1 \right). \tag{3.2}$$

Here $N_{nf}$ is the number density of flow-induced nuclei and $g_n$ is a scaling parameter which depends on temperature and pressure [117], and presumably also the chemical properties of the material, such as isotactity and the presence of nucleating agents. $\Lambda_{\text{hmw}}$ is average stretch of the long chains in the material, whose evolution during flow can be calculated using a continuum-level rheological model such as the Phan-Thien Tanner [127, 128], Rolie-Poly [129] or eXtended Pom-Pom model [130] if the relevant parameters (e.g. relaxation times) are known. Steenbakkers and Peters [5] tested several
other functions of $\Lambda_{\text{hmw}}$ and found the fourth power to give closest agreement with experimental results. In this study we take the slowest mode of a multi-mode Maxwell spectrum (table 3.1) as representative for the high molecular weight tail. The Rolie-Poly model is used to calculate the stretch of the chains in the flow field. The extra stress is given by

$$\sigma = \sum_i G(B_{e,i} - I)$$  \hspace{1cm} (3.3)

with $B_{e,i}$ the elastic Finger tensor of mode $i$, obtained from the Rolie-Poly differential constitutive equation as given by ref. [129],

$$\frac{dB_{e,i}}{dt} = \mathbf{L} \cdot B_{e,i} + B_{e,i} \cdot \mathbf{L}^T - \frac{1}{\lambda_{\text{rep},i}} (B_{e,i} - I) - \frac{1}{\lambda_{R,i}} \left( 1 - \frac{1}{\Lambda_i} \right) \left( B_{e,i} + \beta \Lambda_i^{2\beta} (B_{e,i} - I) \right),$$  \hspace{1cm} (3.4)

with $\mathbf{L} = \nabla \mathbf{v}$ the rate of deformation tensor, and the stretch parameter

$$\Lambda_i = \sqrt{\text{tr}(B_{e,i})/3}. \hspace{1cm} (3.5)$$

Likhtman et al. [129] found the best agreement with experimental data if convective constraint release was turned off; $\beta = 0$ in Eq. 3.4. Steenbakkers and Peters[5] found that this also gave the most accurate results in the nucleation model. Therefore we take $\beta = 0$.

### 3.3.2 Self-enhancing effect

Ordering events are most likely to occur at the molecules in the high molecular weight tail, as these are more susceptible to be stretched than shorter chains. The ordered structures limit the mobility of these hmw chains, thereby acting as additional entanglements on these chains. Effectively, these cause the relaxation times of the hmw tail of the material to increase with the number of flow-induced nuclei. A self-reinforcing effect is the result: if the material contains a large amount of flow-induced nuclei it will have increased relaxation times, and hence be more susceptible to further flow-enhanced nucleation. This mechanism is captured straightforwardly by;

$$\frac{\lambda_{j,\text{hmw}}}{\lambda_{j,\text{hmw},0}} = (1 + \alpha N_{nf}). \hspace{1cm} (3.6)$$

With $j \in \{\text{rep, R}\}$, the reptation and Rouse time, respectively. $\alpha$ is a scaling parameter.

Zuidema et al. [46] introduced the above as an addition to the core of the model, the core being the coupling between chain stretch and nucleation. The addition was necessary to capture experimental data. Although such a phenomenon would be very hard to measure experimentally, there are clear indications for changes in the rheology of a crystallizing melt during the early stages of crystallization, even when the spherulites are still too small to have a noticeable effect on the viscosity, if the behavior of the material is purely suspension-like [14, 21, 131]. It is obvious that the nuclei do not create the junction points in a percolating network because they are too far apart (with radius of gyration of chains $R_g = 10 - 100$ nm and distance between spherulites $10 - 100 \mu$m), but the mechanism for slowing down of chains involved in nuclei can be of a different nature. For example, one could think of a mechanism of "incubators": local regions around a nucleus where mobility is decreased, where the probability of further nucleation is increased [118].

Additionally, not all structures that are created by flow actually crystallize. There is ample evidence of structures (usually referred to as "precursors") forming that do have a certain kind of
order [4, 132--134], but that are not crystalline/that do not grow into spherulites. These structures might also have an effect the mobility of chains.

Because of the lack of direct evidence, the exact mechanism remains indiscernible. Therefore we use the most straightforward way of representing this effect, in the form of Eq. 3.6. We should note that in the results in this paper this effect, although important, is minor. \( \alpha \) is in the order of \( 10^{-14} \) m\(^3\) and \( N_{nf} \) is maximum \( 10^{14} \) m\(^{-3}\), hence the relaxation time is increased by at most a factor of two. In simulations with stronger flow conditions [5, 46, 49], the effect is more pronounced. Finally, as we show in the section "contributions to the viscosity increase", this effect can not be observed in the viscosity in continuous flow.

3.3.3 Continuous flow

The viscosity increase in our calculations of continuous flow is caused by a combination of two effects. First, the reptation and Rouse time of the high molecular weight tail increases as described above. Second, the material can be viewed as a suspension of soft particles (the growing spherulites) in a viscoelastic matrix (the amorphous melt) [20, 21]. As the spherulites grow, the viscosity of the material increases. For low shear rates, where the nucleation density is close to that of a quiescent melt, the viscosity increase is solely caused by the latter phenomenon. The undisturbed volume fraction of the crystalline phase was modeled using the Schneider rate equations [51], which for isothermal conditions and a fixed nucleation density reduce to the well-known Avrami analysis,

\[
\dot{\phi}_3 = 8\pi \dot{N} \quad (\dot{\phi}_3 = 8\pi N)
\]
\[
\dot{\phi}_2 = G\phi_3 \quad (\dot{\phi}_2 = 8\pi R_{tot})
\]
\[
\dot{\phi}_1 = G\phi_2 \quad (\dot{\phi}_1 = S_{tot})
\]
\[
\dot{\phi}_0 = G\phi_1 \quad (\dot{\phi}_0 = V_{tot})
\]

(3.7)

where \( \dot{N} = \frac{dN}{dt} \) is the nucleation rate and \( G \) is the crystal growth rate, which was obtained from Azzurri [122]. The nucleation rate can be divided into a contribution from flow and from temperature changes,

\[
\dot{N} = \frac{dN}{dt}_f + \frac{dN}{dT}_T
\]

In all results presented in this study \( \dot{T} = 0 \). The total number of nuclei is the sum of the quiescent nucleation density and the flow-induced nuclei obtained from the nucleation model described above, \( N = N_q + N_{nf} \). In the short-term shear experiments presented in this study, \( N_q \) is negligible as it is much smaller than \( N_{nf} \). For continuous flow experiments \( N_q \) was obtained from the experiments with the lowest flow rate, where the flow is assumed to have no influence on the nucleation density. \( V_{tot}, S_{tot} \) and \( R_{tot} \) denote per unit volume the total volume of spherulites, their total surface and the sum of their radii, respectively. The Kolmogorov-Avrami model was used to correct for impingement [39, 40],

\[
1 - \xi = \exp(-\phi_0)
\]

(3.8)

where \( \phi_0 \) is the undisturbed volume of spherulites and \( \xi \) is the volume fraction (or space filling) after correcting for impingement. The space filling of spherulites is used as input in the suspension model used by Steenbakkers and Peters [20] and Roozemond et al.[21], which predicts from crystalline volume fraction the relative dynamic modulus \( f'_G = \frac{G'}{G_0} \) with \( G_0 \) the dynamic modulus of the melt. Further information is given in Appendix 3.B.

The viscosity for the longest mode is calculated using the Rolie-Poly model, taking into account relaxation time increase due to flow-induced nuclei. For the other modes we used linear viscoelastic Maxwell-like behavior to calculate the dynamic viscosity. From the dynamic viscosity, assuming the
Cox-Merz rule holds \[135\], we obtained the shear viscosity. The sum of all modes is multiplied with the relative modulus from the suspension model. For shear, this becomes

$$\eta(t) = |f^*_G| \frac{G_M B_{12}(t)}{\dot{\gamma}} + |f^*_G| \sum_{k=1}^{M-1} G_k \left(\dot{\gamma} \lambda_k^2 \left(\frac{1}{1 + \lambda_k^2 \dot{\gamma}^2} + i \frac{\lambda_k}{1 + \lambda_k^2 \dot{\gamma}^2}\right)\right)$$

(3.9)

with $G_k$ and $\lambda_k$ the shear modulus and reptation time of mode $i$ respectively, $M$ the number of Maxwell modes and $B_{12}$ the 12 component of the elastic Finger tensor from the Rolie-Poly model. For extensional flow we have

$$\eta_E(t) = \frac{G_M (B_{11}(t) - B_{22}(t))}{\dot{\varepsilon}} + |f^*_G| \sum_{k=1}^{M-1} 3G_k \lambda_k \left(1 - \exp\left(-\frac{\lambda_k}{t}\right)\right)$$

(3.10)

where $B_{11}$ and $B_{22}$ are the 11 and 22 components of the elastic Finger tensor.

3.4 Results

First, parameter sets for PB800 and BR200 are determined by fitting results from our model to data from short-term shear experiments which give nucleation density for various shear rates, shear times and temperatures. Next, calculations for continuous flow experiments are presented and compared to experimental data. For grades PB800 and BR200, the same parameter sets as for the short-term shear experiments are used. For PB400 parameters are determined by fitting to the continuous flow experiments.

3.4.1 Short-term shear flow experiments

Figures 3.2 and 3.3 show the nucleation density of PB800 and BR200 after short-term shear at different temperatures. The horizontal axis shows the duration of shear, symbols indicate shear rate. The vertical axis indicates the nucleation density observed during isothermal crystallization after cessation of flow. PB800 was held at the shear temperature to crystallize, BR200 was cooled down to 92 $^\circ$C and crystallization was monitored at that temperature. An Arrhenius-like temperature dependence of $g_n$ was implemented,

$$g_n(T) = g_{n,ref} \exp\left(\frac{E_{a,g}}{R} \left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right).$$

(3.11)

Here, $T$ is the temperature at which flow is applied. Three parameters are now required per material to calculate nucleation density for all experiments: $g_{n,ref}$, the parameter coupling backbone stretch to nucleation rate at a reference temperature, $E_{a,g}$, governing the temperature dependence of $g_n$, and $\alpha$, governing the relaxation time increase due to the physical cross-links generated by the flow-induced nuclei. The reference temperature in Eq. 3.11 was taken to be 100 $^\circ$C in all cases. The three parameters (see table 3.4) were determined by least squares fitting to the short-term shear experiments for PB800 and BR200. Although BR200 appears to be vastly more susceptible to flow-enhanced nucleation (compare 10 s$^{-1}$ at 94 $^\circ$C for PB800 and 0.7 s$^{-1}$ at 100 $^\circ$C for BR200), the parameter values are remarkably close to those of PB800, suggesting that their chemistry is similar and the major difference is their chain length and hence relaxation times. Zuidema et al. [46] proposed scaling the parameter coupling nucleation rate to molecular stretch $g_n$ with the rheological shift factor $a_T$, which was validated by Steenbakkers [118]. In contrast, we find no relation between $g_n(T)$ and $a_T$. PB800, which has a lower flow activation energy than BR200, shows that $g_n$ depends much more strongly on temperature. In both cases the activation energy governing the temperature dependence
Flow-enhanced nucleation of P1B

is higher than for \( a_T \), in the case of BR200 only slightly but for PB800 a factor 2.5. However, in the narrower temperature range investigated by Steenbakkers et al., \( g_n \sim a_T \) might be a sufficiently good approximation. The parameter \( \alpha \), governing relaxation time increase caused by flow-induced nucleation sites is the same order of magnitude for both materials.

![Figure 3.2: Nucleation density versus shear time after short-term shear flow of PB800. Different subfigures are different shear and crystallization temperatures. Symbols indicate experimental data, and solid lines are calculations with the parameters in tables 3.1 and 3.4.](image)

The calculations and experimental data show good agreement. For the majority of shear rates and temperatures the model is able to capture the experimental data quantitatively. At higher shear rates, however, the calculations deviate from the experimental results. Especially the experiments with higher shear rates for PB800 (Figs 3.2(a) and (d)) show a much higher nucleation rate. The performance of the model could be improved by incorporating the distinction between precursors and nuclei, as discussed in the section "Theory". However, the main aim of this work is to validate the modeling framework for continuous flow experiments, which are all in the low shear rate regime. Therefore, we expect this formulation of our nucleation model to be satisfactory for current purposes. For a formulation of the model which is also valid in the high shear rate regime the reader is referred to ref. [5].

Table 3.4: Parameters in the nucleation model, determined by fitting to short-term shear experiments (PB800, BR200) or continuous shear flow experiments (PB400)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>PB800</th>
<th>PB400</th>
<th>BR200</th>
</tr>
</thead>
<tbody>
<tr>
<td>( g_n,\text{ref} ) ( \text{m}^{-3} \text{s}^{-1} )</td>
<td>( 4.9 \cdot 10^{10} )</td>
<td>110</td>
<td>4.1 \cdot 10^{10}</td>
</tr>
<tr>
<td>( E_{a,g} ) ( \text{kJ/mol} )</td>
<td>6.3 \cdot 10^{-14}</td>
<td>2.1 \cdot 10^{-11}</td>
<td>1.0 \cdot 10^{-14}</td>
</tr>
<tr>
<td>( \alpha ) ( \text{m}^{3} )</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
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<td>110</td>
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<td>1.0 \cdot 10^{-14}</td>
</tr>
<tr>
<td>( \alpha ) ( \text{m}^{3} )</td>
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<tbody>
<tr>
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<td>( 4.9 \cdot 10^{10} )</td>
<td>110</td>
<td>4.1 \cdot 10^{10}</td>
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<tr>
<td>( E_{a,g} ) ( \text{kJ/mol} )</td>
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<td>( \alpha ) ( \text{m}^{3} )</td>
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Figure 3.3: Nucleation density versus shear time after short-term shear flow of BR200. Different subfigures are different shear temperatures. The crystallization temperature is 92 °C in all cases. Symbols indicate experimental data, and solid lines are calculations with the parameters in tables 3.1 and 3.4.

**Apparent saturation of nucleation density**

A striking qualitative difference between the two materials is the nonlinearity of nucleation density versus shear time. For PB800 the nucleation density can reasonably accurately be described as linear in shear time, but for BR200 the nucleation density clearly exhibits a high slope for short shear times, which levels off at longer shear times. This phenomenon could be interpreted as saturation, which has been observed in a number of studies [15, 16, 24, 25]. Some authors have hypothesized saturation to be caused by depletion of polymer chains above a certain critical molecular weight [24, 32, 118]. However, in the current experiments the saturation-like behavior can be explained purely from a rheological considerations. Figure 3.4 shows for both materials the stretch of the hmw tail and the resulting nucleation rate for different shear rates at one temperature. As the longest Rouse time for BR200 is much higher than for PB800 (see table 3.3), it takes much longer for the stretch to reach a steady state. Therefore, the overshoot in chain stretch is much larger for BR200 than for PB800. During this overshoot the nucleation rate is higher, as it is directly coupled to chain stretch. Only when the chain stretch reaches steady state, the nucleation rate reaches a constant value. Consequently, the flow-induced nucleation density of PB800 continuously increases (as there is hardly an overshoot in chain stretch), and the data for BR200 distinctly level off (because the nucleation rate is much higher during the overshoot than in steady state). This could be (mistakenly) interpreted as some kind of saturation.
Figure 3.4: Stretch of longest mode ((a) and (b)) and resulting nucleation rate ((c) and (d)) in time. (a) and (c): grade PB800, $T = 94^\circ\text{C}$, shear rates are 2, 5 and 10 s$^{-1}$ and shear times 40, 20 and 15 s, respectively. (b) and (d): grade BR200, $T = 140^\circ\text{C}$, shear rates are 2, 4 and 10 s$^{-1}$ and shear times 20, 15 and 8 s, respectively. Note that the slight slope in stretch after the overshoot is caused by the relaxation time increase caused by flow-induced physical cross-links (Eq. 3.6).

3.4.2 Continuous flow experiments

Continuous shear flow

We validate our modeling framework for continuous flow with continuous shear flow experiments on PB800 performed by ref. [19], using the parameter set that was determined from short term shear flow (see table 3.4). The quiescent nucleation density was fit to the experiment with the lowest shear rate. Calculations and experiments are compared in Fig. 3.5. The model performs well over a range of shear rates of nearly three decades, especially considering the fact that the parameter set was fit to experiments done in a different group with a different experimental technique.

Hadinata et al. [17] performed similar experiments on grade PB400, a grade with a molecular weight between PB800 and BR200. Table 3.4 gives the three parameters in the nucleation model for this material, which were fit to these continuous flow experiments. Calculations and experiments are compared in Fig. 3.6. Calculations capture the experimental data very well over a range in shear rate
of over three decades. The values of the parameters in the nucleation model for PB400 qualitatively differ from those of PB800 and BR200; chain stretch initially causes a lower nucleation rate but the flow-induced nuclei have a stronger effect on increasing relaxation times. The temperature dependence of $g_n$ roughly follows $a_T^2$.

**Contributions to the viscosity increase**

The present model accounts for two effects that can increase the viscosity of the material. First, the volume fraction of spherulites, which have a higher stiffness than the surrounding melt, gradually increases. Second, the relaxation time of the high molecular weight tail increases due to flow-induced nuclei acting as physical cross-links. The latter was implemented on empirical basis, as explained in the section "Theory." If this mechanism proves necessary to predict the experimentally observed viscosity, the present results could indirectly provide evidence for such a mechanism.

The contributions from both effects (relaxation time increase and suspension behavior) for continuous flow of PB400 at 107 °C are presented in Fig. 3.7. We observe that the viscosity increase in the calculations is dominated by suspension-like behavior, the contribution from relaxation time increase is too weak to be noticeable for these flow conditions. Hence these results do not provide evidence that flow-induced nuclei increase relaxation times.
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Figure 3.6: Time evolution of normalized shear viscosity in PB400 for a range of shear rates. Different subfigures are different temperatures. Symbols show measurements, solid lines show calculations with parameters as in tables 3.1 and 3.4.

Continuous extensional flow

Using an extensional viscosity fixture (EVF) fitted to a conventional rheometer, Hadinata et al. performed continuous uniaxial extensional flow experiments on grade BR200 [18]. The morphology created in these experiments is presumably highly oriented, for extensional rates with Weissenberg numbers based on stretch greater than unity for the longest chains, $\text{Wi}_{R} = \dot{\varepsilon} > \lambda_{R}^{-1} > 1$ [111]. Table 3.3 shows values of the longest Rouse time. The measurements in this regime are indicated in open symbols in Fig. 3.8. If the crystalline structure becomes highly oriented the current model does not apply, as it describes only crystallites that grow in three dimensions and form a suspension of spherical particles. Therefore, the results of the present model in these conditions should be regarded with care.

Experiments and calculations show excellent agreement for all extension rates (see fig 3.8). The model should indeed apply for $\text{Wi}_{R} < 1$, but surprisingly the calculations also capture the experiments exceptionally well in the range of strain rates where $\text{Wi}_{R} > 1$ and where Hadinata et al. [18] observed "strain-induced crystallization" (i.e. the viscosity upturn occurring at the same Hencky
Flow-enhanced nucleation of P1B

Figure 3.7: Time evolution of normalized shear viscosity in PB400 for a range of shear rates at 107 °C. Symbols show measurements. Solid lines show calculations with the full modeling framework, dash-dotted lines show contribution from the suspension model, dashed lines show contributions from relaxation time increase due to physical cross-links from flow-induced nuclei.

Figure 3.8: Time evolution of transient extensional viscosity in BR200 for a range of extension rates. Different subfigures are different temperatures. Symbols show measurements, solid lines show calculations with parameters as in tables 3.1 and 3.4. Closed symbols show measurements with Wi<sub>R</sub> < 1, open symbols are measurements with Wi<sub>R</sub> > 1.

strain, independent of strain rate). This remarkable result deserves further explanation. Investigation of the contributions of the simulated viscosity shows that the viscosity upturn at these strain rates is actually not caused by crystallization (see Fig. 3.9). Instead, the viscosity of the longest mode, calculated with the Rolie-Poly model, grows unboundedly because Wi<sub>R</sub> > 1 and hence the long chains
are in the stretching regime.

Figure 3.9: Time evolution of transient extensional viscosity in BR200 for a range of extension rates. Different subfigures are different temperatures. Symbols show measurements, solid lines show the calculated viscosity, purely from linear viscoelastic behavior for all modes but the slowest, and calculation with the Rolie-Poly model for the slowest mode. Nucleation is turned off. Closed symbols show measurements with $Wi_R < 1$, open symbols are measurements with $Wi_R > 1$.

Most likely, the viscosity upturn observed in experiments is not caused purely by this strain hardening, because the long chains are finitely extensible which is not included in the Rolie-Poly model. Hence, at temperatures above the melting temperature, a slight strain hardening could be expected [18], but not nearly the viscosity upturn as observed here. Hence, the current model replicates the experimental results without taking into account the complete physical picture. Including all relevant physics would require a description of the nucleation and growth of oriented structures and a suspension model for cylindrical structures, which is outside the scope of this work. Nonetheless, the current model may give some insight into the mechanism of "strain-induced crystallization". We hypothesize that strain hardening due to stretch and strain-controlled crystallization are strongly related: at the strain that chains enter the stretching regime they act as extremely efficient nucleation sites, causing nearly instantaneous crystallization.

We should note that Hadinata et al. [18] did study strain hardening and found no relation with the sharp viscosity upturn. However, they calculated strain hardening caused by entanglements acting as long chain branches using the molecular stress function (MSF) model [136]. This model does not explicitly calculate chain stretch, which might be the reason that they did capture the initial deviation from the linear viscoelastic envelope but did not see the sharp upturn coinciding with crystallization.

Both Derakshandeh et al. [114] and White et al. [115] also observed the viscosity upturn at constant strain in extensional flow. The former performed experiments on two grades of HDPE, of which the rheology was studied in a different publication [137]. As the onset of the terminal regime is not shown, we are not able to estimate the longest relaxation times. But as both these materials have a high polydispersity index, it is likely that the strain rates in their experiments are in the stretching regime for the long chains.

White et al. [115] observed strain-induced crystallization in extensional flow of isotactic polypropylene. Fig. 2 in their paper shows that the longest reptation time is in the order of 100 s for the material they used, which, following Eq. 3.1, gives an estimate for the longest Rouse time of $\sim1$ s. They observed
strain-induced crystallization for $0.01 \text{ s}^{-1} < \dot{\epsilon} < 0.1 \text{ s}^{-1}$. This is not in the stretching regime for this estimate of the longest Rouse time, and hence this would contradict that strain-induced crystallization is related to chain stretch. However, other authors have shown that for similar materials this method of estimating the longest Rouse time is inaccurate [5, 116].

3.5 Conclusions

A modeling framework was presented to calculate flow-induced nucleation density and the evolution of viscosity under the influence of nucleation-enhancing flow. The model couples nucleation rate to molecular deformation, which is calculated from flow conditions via rheological characteristics, i.e. relaxation times. This intermediate step of calculating molecular deformation from a rheological constitutive model has proven to be vital in understanding flow-induced crystallization experiments.

We have shown that the model provides predictive capabilities in shear as well as extensional flow. Good agreement was obtained with short-term shear experiments on poly(1-butene). By combining the nucleation model with a suspension model, introducing no additional parameters, excellent agreement with the viscosity signal in continuous flow experiments was obtained.

The model provides a tool for interpreting some experimental observations. First, the saturation-like effect in flow-induced number density, at least in the present experiments, can be explained solely from the stress overshoot after flow start-up. Because the polymer chains experience large deformations during this overshoot, the nucleation rate also shows an overshoot before reaching steady state, thus causing a saturation-like effect in flow-enhanced nucleation density. This phenomenon was predicted to be more pronounced in materials with higher relaxation times, which is confirmed by experiments. The saturation level, i.e. the value at which nucleation density seemingly reaches a plateau, is highly dependent on shear rate. Second, we believe the upturn in extensional viscosity, occurring at constant strain during continuous flow, to be caused by chains in the hmw tail entering the chain stretch regime, causing nearly instantaneous crystallization.

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3.A Simplifications with respect to the full model

In this appendix the full nucleation model that was used by Steenbakkers [5] is briefly reiterated, after which we highlight the omissions that result in the simplified version of the model that was used in this paper.

In the full model the deformation of chains spawns flow-induced precursors, which transform into nuclei with a typical timescale \( \tau_{pn} \):

\[
\frac{dN_{pf}}{dt} = g_n \left( \Lambda_{hmw}^4(t) - 1 \right) - \frac{N_{pf}}{\tau_{pn}},
\]

(3.12)

\[
\frac{dN_{nf}}{dt} = \frac{N_{pf}}{\tau_{pn}}.
\]

(3.13)

Here \( N_{pf} \) is the number density of flow-induced precursors, and \( N_{nf} \) is the flow-induced number density of nuclei. The distinction between precursors and nuclei is a necessary one, as [5] discussed, because flow (if sufficiently strong) interferes with nucleation. For this reason, all flow-induced nuclei after short-term flow have the same radius at any point in time, within the resolution of an optical microscope [138, 139]. Also in film drawing it was observed that flow impedes nucleation [140–142]. For this reason Steenbakkers took the time scale for nucleation \( \tau_{pn} \) to be infinite during flow and zero after cessation of flow, i.e. no nucleation during flow and instant nucleation after flow. For continuous flow experiments, where nucleation does in fact occur during flow, because the flow rates are too low to interfere with nucleation, this would have to be modified, to for example

\[
\tau_{pn} = \tau_{pn,Q} \exp \left( \zeta \left( \Lambda_{hmw} - 1 \right) \right),
\]

(3.14)

where \( \tau_{pn,Q} \) is the nucleation time in quiescent conditions, which is expected to be much smaller than the typical time for crystallization. The parameter \( \zeta \) determines how strongly \( \tau_{pn} \) increases with flow. For the limit of no or very strong flow this expression results in what was implemented by Steenbakkers and Peters[5], i.e. \( \tau_{pn} = \tau_{pn,Q} \approx 0 \) in quiescent conditions and \( \tau_{pn} \approx \infty \) during strong flows.

Further, they postulated that only precursors, not nuclei, act as physical cross-links. The relaxation time increase in that case is given by

\[
\frac{\lambda_{ij,hmw}}{\lambda_{ij,hmw,0}} = (1 + \alpha N_{pf}).
\]

(3.15)

Thus the effect on the rheology disappears as soon as the precursors nucleate. This argument was introduced for practical reasons: at some point the influence on the relaxation times of the precursors has to relax, otherwise, when the flow is stopped, the relaxation of chain stretch might be balanced out by the relaxation time increase due to creation of precursors. Consequently, the number of flow-induced nuclei would keep growing to infinity. For a more detailed argumentation the reader is referred to ref. [5].

Simplifications

We choose to omit the intermediate step of nucleation precursors, for the reason that including this step requires two additional parameters (\( \zeta \) and \( \tau_{pn,Q} \) in Eq. 3.14) whilst it does not significantly change the final nucleation density. Moreover, because the shear rates considered in this work are relatively weak, we can get away with assuming that nucleation sites do retain their effect on the relaxation times after nucleation; because the relaxation times increase at most by a factor of two in the current experiments (\( \alpha \approx 10^{-14} \) and \( N_{nf} \approx 10^{14} \)), we have no problems with the number of flow-induced nuclei growing to infinity.
3.B Hardening behavior of iP1B

To account for the viscosity increase with increasing crystalline volume fraction, we use the approach of refs. [20, 21]. The material is considered as a suspension of spheres (spherulites) in a viscoelastic matrix (the melt). The generalized self consistent method (GSCM) for spherical particles is used to calculate the viscosity as a function of volume fraction [93--95]. This model requires as input the ratio of the dynamic modulus of the spherulites, which we take equal to the dynamic modulus of the fully crystallized material, and dynamic modulus of the melt. With these parameters known we can use the GSCM to predict the shear modulus relative to the modulus of the melt at all intermediate crystalline volume fractions,

\[ f_G^*(\xi, \omega) = \frac{G^*(\xi, \omega)}{G^*_{\xi=0,\omega}}. \]  

(3.16)

Where \( f_G^* \) is the relative dynamic modulus, \( \xi \) denotes the volume fraction of crystallites, \( \omega \) is the oscillatory frequency. The reader is referred to ref. [21] for more information on applying the GSCM to crystallizing melts.

Coppola et al. [102] measured the storage and loss modulus of the melt and crystallized material at 109 °C for an iP1B with a molecular weight comparable to that of PB400. The data are reproduced in Fig. 3.10(a). We use these values as input for the suspension model. The prediction of the absolute value of the dynamic modulus relative to the dynamic modulus of the melt at intermediate crystalline volume fractions for all oscillatory frequencies is shown in Fig. 3.10(b).

![Figure 3.10](image-url)

Figure 3.10: (a) Frequency sweep of an iP1B at 109 °C. Squares show pure melt, triangles show crystallized material. (b) Absolute value of dynamic modulus normalized with dynamic modulus of the melt versus relative crystallinity for this iP1B from the 3D GSCM.

The exact values of the ratio between the dynamic modulus of the melt and crystallized material will differ between materials, and hence so will \( f_G^*(\xi, \omega) \). However, at low crystalline volume fractions the suspension model is not very sensitive to changes herein. Because we are only interested in the viscosity increase at low crystalline volume fractions, we expect the GSCM with these parameters to be a sufficiently good approximation. To validate this approach, we apply the GSCM with parameters obtained from Coppola’s data to experimental data presented by ref. [131], who measured the storage modulus of crystallizing PB400. We compare their data with a calculation of the storage modulus with
the GSCM, following heterogeneous spherulitical crystallization [52] for which crystalline volume fraction is given by

$$\xi(t) = 1 - \exp(kt^3),$$

(3.17)

where $\xi$ is the crystalline volume fraction, $t$ is time and $k$ is a rate constant which was fit to the data from ref. [131]. The measurement was performed at 95 °C at an oscillatory frequency of 1 rad/s, corresponding to a frequency of approximately 0.57 rad/s at 109 °C in the data from ref. [102]. The result is presented in Fig. 3.11. Indeed we capture the data quite well at early stages of crystallization, despite the final modulus being under predicted by nearly an order of magnitude. Therefore, we expect this approach to give a good indication of when the viscosity shows an upturn due to crystallization, even though we do not have exact values for the moduli of the melt and crystallized material.

Figure 3.11: Time evolution of storage modulus of PB400 crystallizing under quiescent conditions at 95 °C. Symbols show measurements from ref. [131], the line shows a prediction of the GSCM with crystalline volume fraction from heterogeneous nucleation and spherical growth.
Chapter 4

Flow-induced crystallization studied in the RheoDSC device: quantifying the importance of edge effects

Abstract

Flow-induced crystallization is investigated through short-term shear flow experiments on poly(1-butene) in the RheoDSC device. We demonstrate that the DSC signal shows contributions from spherulitic morphology in the center of the sample and oriented structures at the edge of the sample, the latter seemingly being induced by edge effects at the free surface. It is shown that, although small in terms of volume, the crystallization at the edge has a dominating influence on the measured rheology. We show how these kinds of effects can be recognized in stand-alone rheometric studies of flow-induced crystallization.

4.1 Introduction

Rheometry is a widely used tool to study Flow-Induced Crystallization (FIC), because this technique possesses the combined possibilities to apply flow at elevated temperatures and to indirectly monitor structure development[14, 15]. Such studies have been performed on for example isotactic polypropylene (iPP) [9, 15, 16, 64], polyethylene (PE) [14, 114], isotactic poly(1-butene) (iP1B) [10, 17--19], and poly(lactic acid) (PLA) [13], either using the short-term shear protocol [3], cf. refs. [15, 16], or using continuous shear [17, 19]. It has even been shown that using an appropriate model to link rheological properties and crystalline structure [20, 21], one can extract nucleation density after short-term shear from such experiments [9, 16], thus providing an alternative for studies with in-situ optical microscopy.

The recently developed RheoDSC [72--74], a device that allows a simultaneous combination of in-situ Differential Scanning Calorimetry (DSC) and rheological measurements on the same sample, has proven to be a valuable augmentation to these types of experiments. The DSC signal gives a direct measure for the progress of crystallization via latent heat release. The device was previously used for the study of shear induced crystallization during continuous shear flow at mild rates. Moreover, it was shown that even a weak oscillatory shear can significantly enhance crystallization kinetics [104]. Furthermore, it was used for the validation of a model that calculates rheological properties from crystalline volume fraction [10].

In this work we demonstrate the applicability of the RheoDSC device to short-term shear flow experiments. Simultaneously performing DSC and rheometry, we identified crystallization of the bulk of the sample in spherulitic morphology and oriented crystallization in a small part of the sample, presumably induced by edge effects near the free surface. It is shown that, although by volume the fraction of material crystallized in this morphology is rather small, the influence on the measured rheology is tremendous. Our results have important implications for the analysis of stand-alone rheometric studies of FIC: if edge effects occur (i.e. at high shear rates), the rheometric signal might be representative for material near the edge of the sample only, instead of the whole volume. We show how these effects can be recognized in stand-alone rheometric data.

4.2 Experimental

An isotactic poly(1-butene), grade PB400 (\(M_w=176\) kg/mol, \(M_w/M_n=5.7\), isotacticity=98.8%, supplied by LyondellBasell) [24] was subjected to flow and subsequently analyzed during isothermal crystallization in the prototype RheoDSC device. This instrument was constructed starting from two stand-alone commercial instruments: a Q2000 Tzero™DSC (TA Instruments) and an AR-G2 rheometer (TA Instruments) equipped with a plate-plate geometry. The DSC apparatus uses the Tzero™technology, which allows for the correction of the thermal resistances and capacitances of the various heat flow paths in the cell. The AR-G2 rheometer is a sensitive instrument opening the range of ultra-low torques, which is of importance as the diameter of the measurement geometry is chosen to be of comparable dimension as the DSC sensor (5 mm radius, 350\(\mu\)m sample height, 6.5 mg sample mass). For more details the reader is referred to ref. [72]. Both the rheometric and thermal signals of the RheoDSC device have been validated, as reported by refs. [72--74].

Before each experiment, the thermo-mechanical history was erased by keeping the sample at 200 °C for 10 minutes. The sample was cooled down from 200 °C to 92 °C at 5 °C/min, after which it was kept at 92 °C for 5 minutes in order to reach thermal equilibrium of the setup. After this equilibration time, the sample was subjected to a shear pulse with a duration of 10 s with shear rates from 5 s\(^{-1}\) to 30 s\(^{-1}\) with increments of 5 s\(^{-1}\). The heat flow and rheology were monitored during subsequent
isothermal crystallization until crystallization was complete. The oscillatory frequency was 5 rad/s, with 0.5% strain to prevent any disturbance of the oscillatory shear on the crystallization process.

### 4.3 Results

#### 4.3.1 DSC

Figure 4.1(a) shows the heat flow after baseline subtraction, which corrects for the heat stabilization of the apparatus caused by the thermal mass (rotor and inserts) inside the DSC cell. Time \( t = 0 \) is the end of flow. We observed no indications for crystallization during flow. For low shear rates we observe an exothermal crystallization peak with a maximum around 300 s. For higher shear rates the maximum shifts to shorter times. As this peak is already present at low shear rate, where no orientation is expected [17, 24], we assign this peak to crystallization in an isotropic morphology. The typical time scale of crystallization of such a morphology can be estimated using the Avrami equation for isothermal crystallization of heterogeneously nucleated spherulites[39],

\[
\xi = 1 - \exp \left( -\frac{4\pi}{3} N_{\text{sph}} G^3 t^3 \right).
\]  

(4.1)

With \( \xi \) space filling, \( N_{\text{sph}} \) the number of spherulites and \( G \) the crystal growth rate. At 92 °C, the growth rate of this material \( G = 0.1 \) \( \mu \)m/s [122] and a typical nucleation density for these shear rates \( N_{\text{sph}} \approx 10^{13} \) m\(^{-3}\)[12]. Thus we indeed find a crystallization half time of ~250 s, in accordance with what we see in the experiments. This confirms that this peak originates from crystallization of spherulites.

![Figure 4.1: Heat flow for all experiments after baseline subtraction. (a) shows the full measurement, (b) shows a close-up of the signal at short times after flow. The dashed lines shown for all experiments in (b) show the baseline representing dissipation of stored energy from shear heating (Eq. 4.2). Signals are shifted in vertical direction for clarity.](image-url)
4.3.2 Shear heating

For higher shear rates, a second peak appears at short times (maximum at $t \approx 1$ s), and heat flow shortly after flow is strongly increased with respect to the value in quiescent conditions. We ascribe the latter to shear heating, which increases the temperature of the sample during flow. This additional heat is slowly dissipated after flow, which shows in the DSC signal. To account for this effect and isolate the contributions from crystallization, we subtracted an additional baseline from the DSC signal to account for the shear heating. This baseline, following ref. [104], is of the form

$$\Phi(t) = \Phi_0 \exp\left(-t/\lambda\right),$$

(4.2)

with $\Phi(t)$ the heat flow due to stored energy from shear heating, and $\Phi_0$ and $\lambda$ adjustable parameters that were determined per experiment. The latter, representing the typical time scale of dissipation, is between 13.7 and 19.2 seconds for all experiments. The pre-exponential factor $\Phi_0$ increased with shear rate. This additional baseline is shown for all experiments in Fig. 4.1(b).

The total contribution to the heat flow from shear heating, obtained by integrating Eq. 4.2 over time, is shown in Fig. 4.2(a). The total heat per mass added to the system by shear heating can be calculated with

$$H = \frac{1}{m} \int_0^{2\pi} \int_0^R \int_0^{t_s} \sigma_{12} \gamma_r \, r \, d\theta \, dr \, dt$$

$$= \frac{2\pi t_s}{m} \int_0^R \frac{\gamma \omega r}{k} \left(\frac{\gamma \omega r}{R}\right)^{n+1} \, r \, dr$$

$$= \frac{2\pi t_s k^n+1}{m R^{n+1}} \int_0^R r^{n+2} \, dr.$$  

(4.3)

Here $k$ and $n$ are parameters in a power-law representation of the viscosity of the material, as shown in Fig. 4.2(b). From the above, it follows that the total heat added to the system should scale with $\gamma^{n+1}$, shown by the dashed line in Fig. 4.2(a). Indeed this trend captures the data points quite well, indicating that the baseline that we determined for each experiment is a reasonable depiction of the dissipation of energy generated by shear heating.
Figure 4.2: (a) Total contribution to heat flow from viscous dissipation. Line shows a relation of type $\Delta H \sim \dot{\gamma}^{n+1}$. (b) Steady-state viscosity versus shear rate. Line shows a power law $\eta = k\dot{\gamma}^{n-1}$ with $k = 1.5 \cdot 10^4$ and $n = 0.34$.

Figure 4.3 shows the DSC signal after subtraction of the contribution due to shear heating. Now we more clearly observe, with increasing shear rate, the appearance of the second peak at short times. We consider this peak to be the signature of crystallization of shish-kebabs. An estimate with the Avrami equation for crystallization of shish-kebabs,[52]

$$\xi = 1 - \exp\left(-2\pi LG^2\dot{\gamma}^2\right), \quad (4.4)$$

with $L$ the density of shish (typically $10^{12}$ m/m$^3$ for isotactic polypropylene, which, at least in the point-like regime, shows comparable numbers to P1B [112]), indeed gives a half crystallization time of $\sim 3$ s. Crystal growth rate, which does not depend on morphology, is again denoted by $G$.
Flow-induced crystallization studied in the RheoDSC device

Because the two peaks (from spherulitic and shish-kebabs morphology) are well separated in the time domain (between 3 and 10 seconds the heat flow is zero in all experiments), we can easily determine how much of the sample crystallizes in which morphology. To do so, we calculated the total heat released by each of the processes by time integration over the appropriate time intervals.

\[
\Delta H_{\text{shish-kebab}} = \int_{0}^{t_1} w(t) \, dt
\]

\[
\Delta H_{\text{spherulites}} = \int_{t_1}^{t_\infty} w(t) \, dt.
\]  

(4.5)

With \( t_\infty = 2000 \) s and \( t_1 = 5 \) s. The heat flow measured by DSC after subtraction of baseline and contribution from shear heating is denoted by \( w(t) \). The outcome is presented in Fig. 4.4(a). The heat of fusion of the form II modification of poly(1-butene) was reported to be 58-65 J/g[143], and crystallinity for melt-crystallized poly(1-butene) samples was reported to be in the order of 40 %[122, 144]. Hence the values reported here are in the order of what is expected. The total heat release decreases with increasing shear rate, from 25 J/g at the lowest shear rate to 18 J/g at the highest shear rate, whereas Chellamuthu et al. observed that total crystallinity increased with increasing flow strength[144]. Possibly there is some heat leakage into the rotor of the rheometer, which becomes more noticeable at faster crystallization rates. Moreover, although increasing with shear rate, the amount of shish-kebab remains very low compared to the amount of spherulites for all flow conditions. If we assume that the heat of fusion per unit volume is equal for spherulites and shish-kebabs, at the highest shear rate still only 3% of the total volume is filled with shish-kebabs.
Flow-induced crystallization studied in the RheoDSC device

Figure 4.4: (a) Total heat released by crystallization. (b) Thickness of domain with shish-kebabs.

We can calculate the thickness in radial direction of the layer with shish-kebabs from

\[
d = R \left(1 - \sqrt{\frac{\Delta H_{\text{spherulites}}}{\Delta H_{\text{total}}}}\right)
\]  

with \( R = 5 \) mm the radius of the sample, and \( \Delta H \) from equation 4.5. In Fig. 4.4(b), we have plotted the variation with shear rate of thickness in radial direction of the layer with shish-kebabs. As expected, the layer thickness increases with shear rate. The relation between thickness and shear rate tells us something about the nature of the layer. If there are no disturbances of the flow field, shear rate increases linearly with radial position. In this case, because the shear time is constant in all our experiments, the onset of shish-kebab formation is related to a critical shear rate \( \gamma_c \), corresponding to a radial position for a certain applied shear rate; \( r = \frac{\gamma_c}{\dot{\gamma}_{\text{app}}} R \). This fact was exploited by Mykhaylyk and co-workers to determine the critical flow conditions for shish-kebab formation by performing Small Angle X-Ray Scattering at different positions of such a sample [26, 27]. In this case, the oriented layer thickness in radial direction would increase linearly with increasing applied shear rate. Moreover, having a small amount of shish-kebabs at \( 10 \) s\(^{-1} \) would mean that, at an applied shear rate of \( 30 \) s\(^{-1} \), \( 1 - (10/30)^2 = 89 \% \) of the sample would be highly oriented. This is clearly not the case in our experiments; the layer thickness only increases slightly with shear rate and in all experiments there is some form of orientation.

Therefore, we believe that the oriented morphology in this layer is a result of edge effects. Macosko and co-workers observed that for polymer melts in parallel plate geometries, edge fracture can already occur at shear rates in the order of \( 10 \) s\(^{-1} \) [145, 146]. They related the onset of edge fracture to a critical edge velocity. Edge fracture was observed for edge velocities exceeding \( 5 \) mm/s for their experiments (shearing a PDMS melt with viscosity in the range of \( 10^3 \) Pa s for \( 15 \) s). The critical edge velocity was observed to decrease with increasing viscosity. In our experiments, the edge velocity ranges from 1.75-10.5 mm/s with viscosities in the range of \( 10^3 - 10^4 \) Pa s. Moreover, it is not possible to trim the sample edges in the RheoDSC, which might also negatively affect the critical edge velocity. Therefore it is not inconceivable that edge fracture occurs. This might locally impose deformations strong enough to induce shish formation. Although the effect on the overall crystallization kinetics...
is quite small, this effect can strongly influence the measured rheology. We will come back to this in section 4.3.4.

### 4.3.3 Crystallization kinetics

Figure 4.5(a) shows the evolution of space filling of spherulites averaged over the volume of the sample with isotropic morphology, given by

\[ \xi(t) = \frac{1}{\Delta H_{\text{spherulites}}} \int_{t_1}^{t} w(t') dt', \quad (4.7) \]

where \( \Delta H_{\text{spherulites}} \) was calculated from Eq. 4.5 and again \( t_1 = 5 \text{ s} \). As expected, the speed at which crystallization progresses increases with increasing shear rate, because flow strongly increases the nucleation density. Unfortunately we can not extract quantitative information about the nucleation density from these data, because, being governed by the shear rate, nucleation density depends on radial position. Therefore, the measured space filling gives an average over the whole sample. This also becomes apparent if we make an Avrami plot (Fig. 4.5(b)) of these data, which should give a slope of 3 for crystallization of spherulites. Because the nucleation density is not homogeneous throughout the sample, the usual Avrami analysis (in which nucleation density is constant) does not apply, and we observe slopes between 1 and 2. In Appendix 4.A it is demonstrated that a nonhomogeneous nucleation density can indeed result in Avrami exponents in this range.

![Figure 4.5: (a) Evolution of space filling for all shear rates. (b) Avrami plot of the crystallization of spherulites for all flow conditions.](image)

### 4.3.4 Rheology

Figure 4.6 shows the evolution of the dynamic modulus for all flow rates. Strikingly, the bulk crystallization kinetics do not correlate well to the measured rheology. For the strongest flow condition, space filling reaches 50 % at about 100 s (Fig. 4.5(a)). By that time the dynamic modulus is already close to its final value. Additionally, the first measurement point after shear already shows an increase of up to an order of magnitude with respect to the modulus of the quiescent melt.
Flow-induced crystallization studied in the RheoDSC device

Figure 4.6: Evolution of the absolute value of the dynamic modulus after shear.

Apparently, the measured rheological properties do not correlate well to the bulk crystallization kinetics. This is easily explained from the way in which the modulus is determined in plate-plate rheometry. The device measures the torque, given by \[ T = 2\pi \int_0^R \tau_{12}(r) r^2 \, dr, \] \[ (4.8) \]
with \( T \) the torque, and \( \tau_{12} \) the shear stress. From Eq. 4.8 it becomes obvious that the measured rheological properties are strongly dominated by the material at the edge of the sample (large \( r \)). We can quantify the factor with which torque increases if a layer near the outer edge of thickness \( d \) is solidified while the rest of the material is still in the molten state:

\[
\frac{T(d)}{T_0} = 2 \pi \int_0^{R-d} r^2 k \left( \frac{\dot{\gamma} w}{R} \right)^n \, dr + \mu \cdot 2 \pi \int_{R-d}^R r^2 k \left( \frac{\dot{\gamma} w}{R} \right)^n \, dr
\]

\[ (4.9) \]

With \( k = 1.5 \cdot 10^4 \) and \( n = 0.34 \) power law parameters to determine the viscosity, \( \dot{\gamma} w \) the shear rate at \( r = R \), and \( \mu = 3000 \) \[131\] the ratio between the modulus of the crystallized material and the modulus of the melt. \( T_0 \) and \( T \) are respectively the measured torque for a sample fully consisting of a quiescent melt, and with a solidified layer with thickness \( d \) near the edge of the sample. Because the measured modulus directly correlates to the torque, this is also the factor with which the measured modulus will increase,

\[
\frac{|G^*_{t=0}|}{G^*_{\text{melt}}} = \frac{T(d)}{T_0}.
\]

(4.10)

Figure 4.7(a) depicts \( \frac{T}{R} \) versus thickness of the crystallized layer. Because the term in the integral depends so strongly on \( r \), even a very small layer will strongly increase the measured modulus.
Figure 4.7(b) depicts the first measurement point after flow with calculations from Eq. 4.9 with the layer thickness computed from the DSC signal (Fig. 4.4(b)). The measurements and calculations show excellent agreement, proving that indeed the layer experiencing edge effects has a tremendous influence in the rheological signal.

Figure 4.7: (a) Increase in measured rheology versus thickness of crystallized layer. (b) Increase with respect to melt rheology. Open symbols show the measurements, closed symbols show calculations with Eq. 4.9 where layer thickness is given by Eq. 4.6.

This result is an important indication that these kinds of measurements should be interpreted with great care; the rheological signal is representative of a small section of the material rather than the bulk, and experimental issues affecting this layer may severely bias experimental results. Vega et al. also observed this particular fact in a conventional rheometer [147], at shear rates of 60 s\(^{-1}\), which in our view is a strong indication that edge effects have occurred and that the rheological signal should be interpreted with great care. Such artefacts may however be more prevalent in the current experiments than in others, because it is not possible to trim the sample edges in the RheoDSC.
4.4 Conclusions

Flow-induced structure formation in poly(1-butene) was investigated by means of short-term shear flow experiments in the RheoDSC device. It was found that the DSC signal reliably shows crystallization kinetics of the sample. For the investigated flow conditions, the large majority of the sample (>97% by volume) crystallized in the spherulitic morphology. The speed at which crystallization progressed, indicative of the number density of spherulites, consistently increased with shear rate. A small fraction of the sample (<3% by volume) crystallized in the shish-kebab morphology. Because the torque that is used to determine the modulus in plate-plate rheometry is strongly dominated by the material near the edges, this material strongly affects the measured rheology. The unique combination of rheometry and DSC in one device allowed us to quantify these effects. The results obtained indicate that rheological studies on flow-induced crystallization should be interpreted with care, especially at high shear rates when edge fracture may occur, thus severely enhancing the amount of deformation experienced by the material at the edges with respect to the bulk of the sample. The occurrence of these edge effects is signaled by an increase in modulus before the bulk of the sample crystallizes.

Acknowledgements

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4.A Average crystallization kinetics

Because the shear rate is not homogeneous throughout the sample, neither is the flow-induced nucleation density. Therefore the crystallization kinetics measured with DSC are actually an average over the whole sample. Consequently, the Avrami equation for spherulites (Eq. 4.1) does not give a good representation of crystallization kinetics measured with DSC. In this Appendix we qualitatively show how this can result in exponents smaller than 3 in an Avrami plot.

The average crystallization kinetics of a cylindrical sample in which the nucleation density depends on shear rate, with crystallization kinetics in each point given by the Avrami equation for spherulites (Eq. 4.1) are given by

$$\xi_{avg}(t) = \frac{2\pi}{\pi R^2} \int_0^R \left[ 1 - \exp\left(-\frac{4\pi}{3} N(r) G^3 t^3\right) \right] r \, dr,$$

where $N(r)$ is the nucleation density distribution in radial direction. For different distribution functions, the average space filling and its corresponding Avrami plot are shown in Fig. 4.8. Indeed, the slope in the Avrami plot is smaller than 3. This is quite easy to understand: material near the edge of the sample, with high nucleation density, already reaches impingement whereas material in the center of the sample is just starting to crystallize. Therefore the average crystallization kinetics cannot be described with a simple equation.

![Figure 4.8](image-url)

Figure 4.8: (a) Average crystallization kinetics for a sample with a distribution of nucleation density across radial direction. (b) Corresponding Avrami plot.
Chapter 5

Multi-morphological crystallization of shish-kebab structures in isotactic polypropylene: quantitative modelling of parent-daughter crystallization kinetics

Abstract

A model is presented for the crystallization kinetics of flow-induced shish-kebab structures in isotactic polypropylene. The model accounts for two phenomena that affect the crystal growth of kebab structures. First, the temperature of the material increases due to latent heat release. Second, polymer chains are deformed in such a way that growth of kebabs (with their c-axis in flow direction) is promoted. Furthermore, we incorporate crystallization kinetics of the daughter morphology which nucleate on the (010) lateral surface of kebabs. The model is validated with in-situ Wide Angle X-Ray Diffraction data from an in-house developed extensional flow device and a modified multi-pass rheometer used to apply a flow pulse in a slit flow geometry. Excellent agreement is found between the model and experimental data, in terms of crystallization kinetics as well as parent/daughter ratio. The well-known Avrami model, in which it is assumed that crystal growth rate is constant, is widely used to analyze (quasi-)isothermal flow-induced crystallization experiments. We show that, because the growth rate of kebabs is strongly time dependent due to temperature and orientation effects, this analysis fails for experiments like the ones presented in this study. This is manifested in non-integer Avrami coefficients typically smaller than 2, which have been observed in a number of different studies. The current model explains these observations.

5.1 Introduction

Semi-crystalline polymers, such as isotactic polypropylene (iPP) and polyethylene (PE) are widely used in a large variety of products. Because these polymers are processed from the molten state, the flow field acts as unavoidable factor that can change the kinetics and morphology of crystallization and consequently affect the ultimate structure and properties. In order to optimize processing conditions, as well as create products with tailored properties, it is vital to have good understanding of the mechanism behind flow-induced nucleation and crystal growth.

A wealth of experimental work has been performed on the subject of flow-induced crystallization [25, 30–32, 43, 148–150]. Most of the experiments were done using the well-known short-term flow protocol [3], in order to obtain well-defined isothermal experimental conditions in which structure formation is separated from crystal growth. Consequently, the effect of flow on structure formation can be studied in detail, because the crystallization kinetics in quiescent conditions can be characterized thoroughly in separate experiments, cf. ref. [151]. Crystallization kinetics are usually probed in-situ with birefringence [3, 25], or either small-angle X-Ray scattering (SAXS), wide-angle X-Ray diffraction (WAXD), or a combination of the two [30–32, 43, 44, 148, 149]. These types of experiments can be performed in various geometries, for example a slit flow [3, 30, 31, 149], extensional flow device [43], sandwich type shear cell [24, 152], or Linkam-type or Couette shear cell [32, 148, 150]. Well defined experiments with high deformation rates, relevant to processing (∼1000 s⁻¹), can be accomplished most straightforwardly in geometries without free surfaces, e.g. a slit flow, although this geometry has the inherent disadvantage of a non-homogeneous shear rate distribution.

The famous shish-kebab structure, consisting of an extended-chain crystal core (shish) on which disklike folded chain crystals (kebabs) nucleate has been documented in the seminal works by Keller and Pennings [153–156]. In iPP, subject of the present study, an additional morphology, known as daughters, grows epitaxially on the (010) surface of kebabs (in this case also known as parents) [30, 31, 149]. Although qualitatively very well researched, the crystallization kinetics after strong flows are relatively poorly understood. The typical way of modeling the growth of kebabs, as cylinders growing in radial direction, is using the Schneider rate equations [30, 51, 52] combined with the Kolmogorov-Avrami equation [39, 40]. However, this approach fails nearly always [30, 43, 149, 150], which is typically exhibited in Avrami plots slowing slopes of non-integer values, smaller than two. The stronger the flow, typically, the lower the Avrami coefficient. Some authors ascribe this observation to a two-step process (shish growing longitudinally and kebabs that only start growing after a certain induction time)[42]. Other authors hypothesized an altered crystal growth rate during flow with respect to quiescent conditions (cf. the supporting information of ref. [30]).

In this paper we present a model that accurately captures non-integer Avrami coefficients as well as parent/daughter crystallization kinetics. It is important to note there that we do not model the structure formation during flow. Instead, the structure generated by flow is an initial condition from which our model calculates crystallization kinetics. To this end we have adapted the Schneider rate equations to account for temperature increase due to latent heat release, as well as an increased growth rate of parent crystals during and shortly after flow. The model is validated with experimental data from extension flow as well as slit flow, combined with in-situ WAXD. These experiments are presented in section 5.2. In section 5.3 we present the governing equations of the model, followed by validation in section 5.4. In section 5.5 we briefly reiterate the most important conclusions from this work. 
5.2 Experimental

In order to validate our model, we compare calculations with experimental data that were already presented elsewhere [43, 44]. We discuss experiments obtained in two different settings. In both cases the set-up consists of a flow device combined with in-situ Wide Angle X-ray Diffraction (WAXD) to measure crystallinity. In one case the flow set-up is a uniaxial extensional flow device [157]. The other is piston driven slit flow [44]. In both cases the material was a commercial iPP. For the extensional flow experiments the material was kindly supplied by SABIC-Europe, with a weight average molecular weight $M_w = 720$ kg/mol and a number average molecular weight $M_n = 150$ kg/mol. For the slit flow experiments the material is Borealis HD601CF with $M_w = 365$ kg/mol and $M_n = 68$ kg/mol. The short-term flow protocol [3] was used; first thermo-mechanical history is erased above the melting point, after which the material is cooled down to the experimental temperature. At the experimental temperature, a flow is applied with a duration short compared to the time needed to complete crystallization, and crystallization during and after flow was monitored under isothermal conditions.

5.2.1 Extensional flow

The extensional flow experiments were performed at the National Synchrotron Radiation Lab in Hefei, China, using an in-house developed extensional rheometer [157]. The temperature was 138 °C in all cases. The data in this study were obtained at three strain rates; 3.1, 12.6, and 25.1 s$^{-1}$. For each strain rate three flow durations were investigated, to give a total strain of 2.0, 2.5, and 3.0 for all strain rates.

5.2.2 Slit flow

The slit flow experiments [44] were performed at the Dutch-Belgian beamline BM26B (DUBBLE) at the European Synchrotron Radiation Facility ESRF) in Grenoble, France. The flow cell was operated on a modified Multi-Pass Rheometer (MPR) [158], which in this case was solely used to subject the material to a flow pulse in a slit. The experimental temperature was 145 °C in all cases. More information on the experimental conditions is given in table 5.1.

Table 5.1: Experimental conditions in the MPR. Wall shear rate and wall shear stress were calculated at steady state using a Carreau-Yasuda model for the shear rate dependence of the viscosity.

<table>
<thead>
<tr>
<th>Piston speed [mm/s]</th>
<th>Flow duration [s]</th>
<th>Shear rate at wall $\dot{\gamma}_w$ [s$^{-1}$]</th>
<th>Shear stress at wall $\sigma_w$ [x 10$^5$ Pa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>0.25</td>
<td>370</td>
<td>1.21</td>
</tr>
<tr>
<td>80</td>
<td>0.25</td>
<td>500</td>
<td>1.35</td>
</tr>
<tr>
<td>100</td>
<td>0.25</td>
<td>635</td>
<td>1.47</td>
</tr>
<tr>
<td>120</td>
<td>0.23</td>
<td>769</td>
<td>1.57</td>
</tr>
</tbody>
</table>

5.2.3 WAXD analysis

In this paper we compare crystallinity of the parent and daughter species from our calculations and experiments. The crystallinity from experiments is obtained by dividing the area below the 110 peak
of the parents and daughters by the area at complete space filling,
\[ \xi_i(t) = \frac{A_i(t)}{A_{\infty,i}}, \]  
(5.1)
where \( i \) can be parent or daughter. \( A_{\infty,i} \) depends on the detector and the thickness of the sample (extension) or shear layer (MPR). Because this thickness is unknown (for the extension experiments one easily make an estimation, but this is not as straightforward as one might think, see section 5.A), we determined \( A_{\infty,p} \), the 110 peak area for 100% space filling of parent crystals, separately for each flow condition. \( A_{\infty,d} \) is related to \( A_{\infty,p} \) via a geometrical correction factor, which depends on scattering angle \([31, 159]\). In this work we do not perform the full geometrical correction. Instead we take a constant factor to relate the two, \( A_{\infty,d} = c_{\text{geometry}} A_{\infty,p} \). The areas parent and daughter crystals are now given by
\[ A_{p,110}(t) = \xi_p(t) A_{\infty,p} \]
\[ A_{d,110}(t) = \xi_d(t) c_{\text{geometry}} A_{\infty,p} \]  
(5.2)
We determined one factor for each type of experiment. For the extension experiments we found \( c_{\text{geometry}} = 3.7 \), for the MPR experiments \( c_{\text{geometry}} = 3.3 \). These values are close to the range \( c_{\text{geometry}} = 3.7 - 4.4 \), found by Ma et al.\([160]\).

All experiments with the MPR were performed twice; once with a Frelon detector with an exposure time of 2 s and azimuthal range of \( > 90^\circ \), and once with a Pilatus detector that has an exposure time of 0.03 s and azimuthal range of \( < 90^\circ \). See figure 5.1. Because the latter has a smaller azimuthal range, only the parent morphology appears in the scattering pattern. The detector used for the extensional flow experiments had an azimuthal range of \( > 90^\circ \). For the data collected with the Pilatus detector, the area of the parent reflection is given by the area underneath the (isotropic) baseline subtracted scattering pattern. Regarding the patterns acquired with the Frelon detector and the data obtained with the extensional flow device, azimuthal scans of the (110) reflection were fitted by Lorentzian peaks to calculate the area of both the parent and daughter lamellae reflections. Examples of procedures for both detectors are given in Fig. 5.1. For further information about the WAXD set-ups the reader is referred to refs. \([43, 44, 157]\).

### 5.2.4 Depth sectioning

The inherent disadvantage of the slit flow geometry is the non-uniformity of shear stress and rate along the thickness. Consequently, there will also be a variation in crystalline structure in thickness direction; highly oriented, densely packed shish near the wall and isotropic structure near the center of the slit. Therefore the measured crystallinity from WAXD is effectively an average over the slit thickness. Fernandez-Ballester et al. proposed the "depth-sectioning" method \([31]\) to correct for this. We use the method to extract the crystallization kinetics of only the shear layer near the wall from the diffraction patterns, which otherwise probe an average of the crystallization kinetics over the slit thickness.

The concept of the depth-sectioning method departs from the linear variation of local shear stress with position from the center \( x \). Given two experiments, with piston speeds \( v_{\text{pist},1} \) and \( v_{\text{pist},2} \) and corresponding wall shear stresses \( \sigma_{w,1} \) and \( \sigma_{w,2} \), with \( \sigma_{w,2} > \sigma_{w,1} \). Then the stress history for experiment 1 for positions \( 0 < x < \frac{d}{2} \) will be the the same as the stress history in experiment 2 for positions \( 0 < x < \frac{\sigma_{w,1} d}{\sigma_{w,2}} \). If crystal structure is a function of only shear stress, the contribution to the WAXD signal from the crystalline structure in experiment 2 for \( \frac{\sigma_{w,1} d}{\sigma_{w,2}} < x < \frac{d}{2} \) is given by
\[ A_{2-1} = A_2 - \frac{\sigma_{w,1}}{\sigma_{w,2}} A_1, \]  
(5.3)
with $A_1(t)$ and $A_2(t)$ the 110 areas from WAXD for experiments 1 and 2, respectively. To make a fair comparison between different flow conditions one has to normalize the signal for layer thickness. The final 110 areas from depth sectioning then become

$$A_2 - 1 = \frac{A_2 - A_1}{1 - \sigma_{w,1}/\sigma_{w,2}}. \quad (5.4)$$

In this way we extract crystallization kinetics from only highly oriented shish-kebab from the data, which would otherwise also contain the crystallization kinetics of the core layer, which will also contain crystallization of spherulites. As is shown in table 5.1, the ratios of shear stresses between different flow conditions is approximately 0.95 in all cases. Hence, the layers of which we calculate the crystallization kinetics typically fill 5% of the thickness of the slit.

In this paper we have used data from four piston speeds for validation purposes. The areas below the 110 peak of parent crystals are given in figure 5.2(a). Corresponding steady-state shear rates and shear stresses at the wall, calculated using the finite element code presented in Chapter 7, are given in table 5.1. Using the depth-sectioning technique, we have converted these data into information about three layers. This is shown in figure 5.2(b).
Figure 5.2: Area below 110 peak for parent crystals for different piston speeds. (a) Before depth sectioning, (b) after depth sectioning.

Note: the depth sectioning method is just an approximation in this case, as (1) pressure effects are not taken into account, (2) we neglect start-up behavior, which shows different time scales for different piston speeds, and (3) the shear times for 120 mm/s and 100 mm/s differ slightly (0.25 s and 0.23 s, respectively). However, as can be see in figure 5.3 which shows the pressure drop over the slit geometry, the timescale for start-up of flow is close for all piston speeds, as is the pressure. Moreover, figure 5.2(b) shows that all data end more or less in a plateau, indicating that indeed the crystallization kinetics of morphologies with less dense crystal structure have been filtered out.

Figure 5.3: Evolution of pressure drop over the slit for different piston speeds.
5.3 Model

Paramount to accurately describing crystallization kinetics is accurately calculating the crystal growth, which changes in time due to (1) orientation of the material and (2) temperature, the latter of which increases during crystallization due to latent heat release. In this section we present the modeling framework to do so.

5.3.1 Geometry

The equations presented in this work are solved on a 1D geometry representing half of the sample, as depicted in figure 5.4. The X-Ray beam traverses across the sample in x-direction. The center of the sample is at \( x = 0 \). At \( x = d/2 \) the polymer is in contact with the surroundings; in the case of extension experiments the polymer-air interface, and in the slit flow experiments the polymer-steel interface. At both these points we must prescribe appropriate boundary conditions on the temperature. The thickness of the sample in the slit flow geometry is always the same, \( d/2 = 0.75 \) mm, whereas it starts at \( d/2 = 0.5 \) mm and decreases with increasing strain in the extension experiments. As was shown by Nielsen et al. [161], the sample dimensions govern if the deformation is uniaxial or biaxial extension, and hence how the thickness decreases exactly with strain. We will come back to this in section 5.A.

Figure 5.4: Schematic depiction of a sample in (a) the extensional flow device and (b) the MPR.

5.3.2 Energy equation

To calculate the temperature distribution in the material the heat balance is solved,

\[
\rho c_p \frac{\partial T}{\partial t} = \lambda \frac{\partial^2 T}{\partial x^2} + \rho \chi_\infty \Delta H \frac{\partial \xi}{\partial t} + \sigma : \mathbf{D},
\]

with \( \rho, c_p, \lambda, \chi_\infty, \) and \( \Delta H \) material parameters as given in Table 5.2. The latent heat of crystallization \( \Delta H \) is multiplied with the final crystallinity of the material \( \chi_\infty \) to account for the fact that the material is not fully crystalline. \( T \) is temperature, \( t \) is time, and \( \xi \) is crystalline volume fraction, the modeling of which is described in section 5.3.3. Heating due to viscous dissipation is accounted for by the term \( \sigma : \mathbf{D} \). Because we calculate crystallization kinetics after flow, this term is zero during crystallization. However, viscous dissipation does affect the initial temperature distribution in the slit flow experiments. Therefore the initial temperature distribution was calculated with a finite element
Multi-morphological crystallization of shish-kebab structures in iPP code which is described in detail in Chapter 7. In the extension experiments the deformation rates are much smaller, and thus this term can be neglected.

| Table 5.2: Material parameters for the heat balance |
|---------------------------------|----------|-----------------|
| quantity                        | symbol   | value [unit]     |
| density (polymer)               | \(\rho_p\) | 800 [kg/m\(^3\)] |
| heat capacity (polymer)         | \(c_{p,p}\) | 3157 [J/kgK] |
| heat conduction coefficient (polymer) | \(\lambda_p\) | 0.11 [W/mK] |
| final crystallinity             | \(\chi_\infty\) | 65 [%] |
| heat of crystallization         | \(\Delta H\) | 207 [J/g] |
| density (steel)                 | \(\rho_s\) | 8000 [kg/m\(^3\)] |
| heat capacity (steel)           | \(c_{p,s}\) | 670 [J/kgK] |
| heat conduction coefficient (steel) | \(\lambda_s\) | 80 [W/mK] |

**Boundary conditions**

The heat balance requires two boundary conditions on the temperature. In the center of the sample (at \(x = 0\)), no flux boundary conditions are prescribed;

\[
\frac{\partial T}{\partial x} = 0. \tag{5.6}
\]

For the extension experiments, a Robin boundary conditions is prescribed at the polymer-air interface (\(x = d/2\)),

\[
\lambda \frac{\partial T}{\partial x} = h(T - T_\infty), \tag{5.7}
\]

where \(T_\infty\) is the temperature of the air in the oven and \(h = 100 \text{ W/m}^2\text{K}\) is the typical heat transfer coefficient of convected air [162].

The MPR has thermocouples embedded in the steel, 0.5 mm away from the polymer (see figure 5.4(b)). The temperature of these thermocouples remained constant during flow and subsequent crystallization. We use this information for the boundary condition in the slit flow geometry. The energy balance is also solved for the steel between the polymer and the thermocouples, and we prescribe a Dirichlet boundary condition at the place of the thermocouples,

\[
T = T_\infty. \tag{5.8}
\]

**5.3.3 Crystallization kinetics**

Strong flows create fibrillar crystalline structures (shish). The length per unit volume of shish, denoted by \(L\), is assumed to be constant after cessation of flow. So-called "kebabs", also known as parent lamellae, grow radially outward from the shish. On their (010) lateral surface another species of lamellae, known as daughters, nucleate [31, 134]. Figure 5.5 depicts the three morphologies in a schematic way.
Figure 5.5: Schematic depiction of a shish (grey) with parent kebabs (red) and daughter lamellae (blue). The surface area of kebab on which both parent and daughter morphology can grow is denoted by $\psi_{1,p}$.

**Crystal growth rate**

Due to the speed at which crystallization progresses in the conditions of interest for this paper, the heat released during crystallization cannot be diffused fast enough to keep the sample at isothermal conditions. Therefore the temperature dependence of the crystal growth rate needs to be accounted for. The growth rate in quiescent conditions can be calculated with

$$G_q = G_{\text{ref}} \exp(-c_G(T - T_{\text{ref}})^2),$$

(5.9)

where $G_q$ is the crystal growth rate in quiescent conditions, and $G_{\text{ref}}$, $c_G$, and $T_{\text{ref}}$ are parameters given in Table 5.3. These parameters were measured for the grade of iPP that was used in the MPR experiments. Since the crystal growth rate of iPP homopolymer shows little dependence on molecular weight [16, 151, 163], we also use these parameters for the calculations on the extension experiments.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Symbol</th>
<th>Value [unit]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum crystal growth rate</td>
<td>$G_{\text{ref}}$</td>
<td>4.5 $\mu$m/s</td>
</tr>
<tr>
<td>Growth rate temperature dependence</td>
<td>$c_G$</td>
<td>$2.3 \cdot 10^{-3}$ [1/K]</td>
</tr>
<tr>
<td>Reference temperature</td>
<td>$T_{\text{ref}}$</td>
<td>363 [K]</td>
</tr>
</tbody>
</table>

Additionally, some authors suggest the growth of parent lamellae is promoted during the flow pulse and relaxation afterwards, because chains are oriented in the c-axis direction of their unit cells [30, 42]. In time, this effect would relax and crystal growth rate would go to the quiescent value. Furthermore, one could imagine that chains that are tethered to the shish backbone, so-called "hairs" [164], crystallize at higher rate than chains in the melt, because their mobility is restricted. This would result in a growth rate that depends on kebab radius instead of time.
At the moment we can not distinguish which of the two effects (or both) plays a role. Therefore we account for the combination of the two with an empirical relation. During flow the growth rate is increased with a factor $\mu_{\text{flow}}$. At the start of crystallization, coinciding with the end of flow, this effect relaxes due to chains relaxing towards their equilibrium conformation. This happens with a timescale $\lambda_G$:

$$G_p(t, T) = G_q(T) \left[ 1 + \mu_{\text{flow}} \exp(-t/\lambda_G) \right]. \quad (5.10)$$

Where $G_p$ is the growth rate of parent lamellae, $\mu_{\text{flow}}$ is the additional growth rate due to flow and $\lambda_G$ is the relevant time scale, $t$ is the time since the cessation of flow. In the present experiments, we found $\mu_{\text{flow}} = 4$ (in the same order as ref. [30], who hypothesized $\Delta \mu_{\text{flow}} = 10$). The time scale with which the effect relaxes $\lambda_G$ is 6 s in the extension experiments and 9 s in the slit flow experiments, which are in the same order as the relaxation time for an average mode or the relaxation time for chain stretch of the high-molecular weight tail. The time scale for relaxation of this effect $\lambda_G$ is higher in the slit flow experiments, which is unexpected because the material in these experiments has a lower molecular weight than the material in the extension experiments. At the moment we can not offer an explanation for this observation.

The flow-induced conformation makes crystallization in the daughter morphology less preferable. However, because growth of daughter crystals only becomes noticeable when the chains have relaxed to their equilibrium conformations, we take the growth rate for this species always equal to the quiescent growth rate,

$$G_d(T) = G_q(T). \quad (5.11)$$

Crystallization kinetics

The Schneider rate equations [51] have been well established to accurately describe crystallization kinetics in quiescent conditions. Similar to the approach taken by Eder [52], we have taken the Schneider rate equations as a point of departure to formulate a model that calculates the volume fractions of parents as well as daughter crystals. In this paper we propose an addition to these equations for the daughter species. For the parents we have

$$\psi_{2,p} = 4\pi L_{\text{tot}},$$
$$\partial_t \psi_{1,p} = G_p \psi_{2,p},$$
$$\partial_t \psi_{0,p} = G_p f_p \psi_{1,p}. \quad (5.12)$$

Here $L_{\text{tot}}$ denotes the total length of shish per unit volume and $G_p$ is the crystal growth rate of parent species. $\psi_{2,p}$, $\psi_{1,p}$, and $\psi_{0,p}$ are measures for the shish length per unit volume, the surface area of kebabs, and undisturbed volume of kebabs, respectively. The volume fraction of the shish itself is neglected, because it is very small compared to the total volume of shish-kebabs (the radius of a shish is in the order of 10 nm [164] while the radius of a shish-kebab grows up to about 100 nm (cf. ref. [112] and Chapter 6 of this Thesis).

From our picture of the shish-parent-daughter morphology (Fig. 5.5), it follows that daughter lamellae nucleate on the surface of the parents. Therefore we propose that the evolution of the volume fraction of daughters scales with the area of the parents,

$$\partial_t \psi_{0,d} = G_d f_d \psi_{1,p}, \quad (5.13)$$

where $\psi_{0,d}$ is the undisturbed volume fraction of daughters. The total surface area of kebabs, denoted by $\psi_{1,p}$ (see Fig. 5.5), is obtained from Eq. 5.12. In our model, the lateral surface of the parents
acts as nucleation site for both parents and daughters. Here too it is important that during flow the crystallization of parent crystals is promoted. The parent and daughter morphologies compete for the same nucleation sites. To account for the favorability of one or the other, these nucleation sites are allocated to either parent or daughter morphology based on their their momentary growth rates;

\[ f_p = f_{p0}(T) \frac{G_p}{G_p + G_d} \]
\[ f_d = f_{d0}(T) \frac{G_d}{G_p + G_d}. \]  

(5.14)

Where \( f_{p0} \) and \( f_{d0} \) determine the parent/daughter ratio in quiescent conditions, which may depend on temperature [165, 166]. In experiments with conditions relevant to the current experiments, it has been observed that the parent/daughter ratio is close to unity for low flow rates [31]. Therefore we take \( f_{p0} = f_{d0} = 1 \) in all cases. Because \( f_p \) and \( f_d \) depend on growth rate, during flow, when the crystal growth rate of parents is increased with respect to the quiescent value, more surface of the kebabs is assigned to nucleate parent crystals. A similar model for the allocation of nucleation sites to different crystal phases of iPP was also used by van Drongelen et al. [151]. It is important to note that the proposed mechanism is a minimal model to test the influence of changing growth rate and daughters nucleating on parents; it may be an oversimplification of the actual physics.

To correct for impingement, we use the well-known Kolmogorov-Avrami equation [39];

\[ \xi = 1 - \exp \left( -\psi_{0,p} - \psi_{0,d} \right), \]  

(5.15)

where \( \xi \) is the crystalline volume fraction, or space filling. From Eq. 5.15 follows that the respective volume fractions of parents and daughters are given by

\[ \partial_t \xi_p = (1 - \xi) \partial_t \psi_{0,p}, \]
\[ \partial_t \xi_d = (1 - \xi) \partial_t \psi_{0,d}. \]  

(5.16)
5.4 Results

In this section we present results from calculations with the current model. First, we show some simulations to highlight the important physics in the model. Next, we compare crystallinity and parent/daughter ratio from our model to experimental data.

5.4.1 Influence of input parameters on modeling results

The key experimental observations that can be explained with the current model are (1) crystallization kinetics that do not adhere to standard Avrami kinetics, and (2) the ratio of parent to daughter crystals which increases with flow strength. The first of these is caused by the fact that crystal growth rate is not constant; it changes due to orientation or stretch of chains and temperature, which increases due to latent heat release. The second phenomenon is a result of the fact that parent and daughters compete for the same volume, combined with the effect of flow on the growth rate of parents.

The above mentioned features are illustrated by the results presented in this section. The conditions and geometry are those of the extension experiments described in section 5.3.1.

The shish length per unit volume $L_{\text{tot}}$ is varied. Figure 5.6 shows the evolution of crystallinity of parents (a) and daughters (b). The inserts show Avrami plots. Figure 5.7(a) shows the parent/daughter ratio, i.e. $\xi_p(t)/\xi_d(t)$. Figure 5.7(b) shows the temperature in the center point of the sample.

![Figure 5.6: Crystallinity for parents (a) and daughters (b) in time from simulations with varying shish length. Inserts show Avrami plots.](image)

The trends described above are clearly visible; with increasing shish density, crystal growth progresses faster. Therefore a larger part of the space is filled during or shortly after flow, when the growth rate of parent crystals is higher than the growth rate of daughter crystals. Consequently the final parent/daughter ratio increases. Moreover, due to the changing growth rate of parents and increasing temperature, the Avrami coefficients are smaller than two.

For the lowest shish density shown, a negligible part of space is filled during this time. As a result the parent/daughter ratio is equal to unity. Furthermore, the crystallization progresses slowly enough that the sample can lose nearly all the latent heat released during crystallization to the surrounding air, resulting in an Avrami coefficient of close to two.
Multi-morphological crystallization of shish-kebab structures in iPP

5.4.2 Validation

In this section we compare calculations and experiments. It is important to stress that for each separate flow conditions, we have one adjustable parameter in the model, the shish length per unit volume \( L_{tot} \). Therefore, this model can be used not only to explain crystallization kinetics, but also to extract information about shish density from the experimental data.

Extension experiments

Calculations and experiments are compared in terms of area of the 110 peak in figure 5.8. The calculations capture the experimental data quite accurately. Note that for higher strain rates and strains, the final volume fraction of parents increases at the cost of the daughters. As we pointed out earlier, this is a result of the increased growth rate of parents during flow (Eq 5.10); during a short time after flow the growth of parents is faster than growth of daughters. If the majority of the space is filled during this time, parents will be more abundant than daughters because they compete for the same volume.

Figure 5.7: (a) Parent/daughter ratio for different shish lengths per unit volume. (b) Temperature evolution in the center of the sample.
Figure 5.8: Area below 110 peak for parents (top row) and daughters (bottom row). Figures from left to right show increasing strain rate. Different symbols/line types are different strains. Symbols show measurements, lines indicate calculations.

Figure 5.9: Parent/daughter ratio for experiments with different strain rates. Symbols show measurements, lines indicate calculations.

Figure 5.10 shows the shish length per unit volume for all experiments determined in this way. The values shown are in the order of magnitude of what is expected for such flow conditions and increase with increasing strain and strain rate, as expected [49, 112].
Figure 5.10: Values of the shish length per unit volume $L_{tot}$ for different strains and strain rates, obtained from fitting the calculations to experimental data. Lines are to guide the eye.

**Slit flow**

In this section experimental data obtained in the MPR are compared with calculations with the model. The shear rates in these experiments are exceedingly high (see table 5.1). Consequently, viscous heating has to be taken into account because it significantly affects the temperature of the material at the start of crystallization. We calculated this temperature distribution with the finite element code described in Chapter 7 and used this as the initial value of the temperature in the slit. The initial temperature distribution is shown in figure 5.11(a).
After depth sectioning, we have data for the crystallization experiments in the shear layer(s) for three experiments. We take the shish length per unit volume to be constant within each shear layer. Outside the shear layers no crystallization takes place. The shish length is fit to each experiment separately, starting with the lowest piston speed. For higher piston speeds, there are multiple shear layers, see figure 5.11(b). This is important because the heat release in the shear layers close to the center slow down the crystallization kinetics the outermost shear layer. Note, that we fit the shish length to the crystallization kinetics of the parents. The crystallization kinetics of the daughters and parent/daughter ratio are predictions.

Figure 5.12: $A_{110}$ in the MPR experiments for (a) parents and (b) daughters. Symbols show measurements, lines show calculations. Insert are Avrami plots.
The crystallization kinetics for both parents and daughters from experiments and calculations are compared in figure 5.12. Figure 5.13(a) shows the parent/daughter ratio. The crystallization kinetics, as well as the evolution of the parent/daughter ratio are quantitatively captured by the model. Figure 5.13(b) depicts the shish length for each flow condition. The values show the trend that we expect, i.e. increasing with piston speed. These values, \( L_{\text{tot}} = 10^{12} - 10^{13} \text{ m/m}^3 \) correspond to shish that are in the order of 300 nm to 1 \( \mu \)m apart. Seki et al. found roughly the same values\[112\]. At long times in the weakest flow condition there is a large discrepancy between the crystallization kinetics of the daughters in calculations and experiments; the experimental data do not show a plateau whereas the calculations do. Possibly the cause of this can be found in crystallization outside the shear layer which was not completely filtered out by depth sectioning.

![Figure 5.13](image)

Figure 5.13: (a) Parent/daughter ratio for the MPR experiments. Symbols show measurements, lines show calculations. (b) Specific shish length for MPR calculations.
5.5 Conclusions

We presented a model that, for the first time, accurately captures multi-morphological crystallization kinetics of shish-kebab structures in iPP. The model provides explanations for two features widely observed in experiments.

First, the temperature changes because of latent heat release, and flow deforms chains in such a way that crystallization of parent morphology (with c-axis in flow direction) is promoted. Consequently, the crystal growth rate changes during crystallization. In this case the classical Avrami analysis no longer applies, resulting in the widely observed non-integer Avrami coefficients.

Second, parent and daughter lamellae both nucleate on the surface area of shish-kebabs, and they compete for the same volume. During and shortly after flow, crystallization of parent crystals is promoted. Although this effect relaxes quite rapidly after flow (timescale in the order of 10 seconds), the space filled during this time contains considerably more parents than daughters. Therefore, the parent/daughter ratio increases with shish density, and therefore with flow strength/duration.
5.A Final peak areas in extension

The area below the 110 peak of the parent crystals at 100% space filling, $A_{\infty,p}$, for the extension experiments deserves some further investigation. These are shown for all flow conditions in figure 5.14(a). It is commonly observed\[31, 44\] that $A_{\infty,p}$ increases with increasing strain. However, our data show it decreases with increasing strain. The cause of this observation can be found in the decreasing thickness of the sample with increasing strain. Hence, one would expect that a clear trend emerges when these are corrected for the decreasing thickness with increasing strain, for uniaxial deformation given by

$$d = d_0 e^{-\varepsilon/2}. \quad (5.17)$$

The areas after correction are shown in figure 5.14(b). Even after this correction, no clear trends become visible. However, the thickness calculated using Eq 5.17 might not be the actual thickness of the sample. The group of Hassager performed some tests with a similar extensional rheometer as the present one and found that already for aspect ratios (height/thickness) in the order of 10, the deformation is closer to biaxial rather than uniaxial \[161\]. As the aspect ratio in the current experiments is 18, this is something that has to be taken into account. Therefore we also tried normalizing the final areas with a thickness that would result from biaxial stretching:

$$d = d_0 e^{-\varepsilon}. \quad (5.18)$$

These results are shown in figure 5.14(c). Now we do observe a clear trend: the peak of parents increases with increasing strain. This indicates that indeed the deformation is not perfectly uniaxial, and probably at higher strains is closer to biaxial. Therefore the thickness of the sample, which is used as dimension of the grid to solve the energy balance, might be inaccurate. This does have an effect, but calculations with sample thickness decreasing according to biaxial deformation have shown that this effect becomes noticeable only at the highest strains, and it can be corrected for by increasing $L$.\[72\]
Figure 5.14: Final peak areas of the parent crystals $A_{p,\infty}$ in the extension experiments. (a) shows the uncorrected values, (b) shows the values corrected for a decrease in thickness from uniaxial deformation, (c) shows the values corrected for a decrease in thickness from biaxial stretching. Lines are to guide the eye.
Chapter 6

Self-regulation in structure formation

Abstract

Flow-induced structure formation is investigated with in-situ Wide Angle X-Ray Diffraction with ultra-high acquisition rate (30 Hz) using isotactic polypropylene in a piston driven slit flow with high wall shear rates (up to $\sim 900 \text{ s}^{-1}$). We focus on crystallization within the shear layers that form in the high shear rate regions near the walls. Remarkably, the kinetics of the crystallization process show no dependence on either flow rate or flow time; the crystallization progresses identically regardless. Stronger or longer flows only increase the thickness of the layers. A conceptual model is proposed to explain the phenomenon. Above a certain threshold, the number of shish-kebabs formed affect the rheology such that further structure formation is halted. The critical amount is reached already within 0.1 s under the current flow conditions. The change in rheology is hypothesized to be a consequence of the "hairy" nature of shish. Our results have large implications for process modelling, since they suggest that for injection molding type flows, crystallization kinetics can be considered independent of deformation history.

6.1 Introduction

Flow-induced crystallization in polymer processing determines to a great extent the final product properties [2, 109]. Especially at relatively low temperatures, i.e. between the melting point of crystals as measured during heating, and the crystallization temperature measured upon cooling, flow increases the number of nucleation sites, causing fine structures in the product’s morphology. If the flow is strong enough, it can even create anisotropic crystalline structures, known as shish-kebabs. These structures, consisting of a fibrous backbone with lamellar overgrowth, were first recognized in notably stirred undercooled solutions [155, 156], and later also in polymer melts [154]. Extensive research has been directed to the precise morphology of shish-kebabs. It was found that the shishes consist of regions of extended chain crystals connected by fringe-like amorphous regions, with kebabs formed by folded chain lamellae growing radially outward [156, 164]. A number of studies were directed to the minimal flow conditions needed to create these structures, expressed either in terms of stress [30], mechanical work [4, 26, 28], or backbone stretch [46, 49]. Long chains, although their concentration in shish-kebabs is not higher compared to the rest of the material [37], were proven to play a catalytic role in the formation of shish-kebabs [22, 30, 46]. Chain stretch being a prerequisite, decreasing mobility with molecular weight promotes the formation of shishes. The mechanism behind the longitudinal growth of shish also got attention. Because "point-like" nuclei \(^1\) have been observed to appear before the formation of oriented structures [52], it has been hypothesized that chains that are convected past the existing precursor, "streamers", are tethered onto the nucleus and hence propagate the shish in lengthwise direction [22], or that "point-like" nuclei align and merge together, forming a shish [36]. The difficulty in studying the growth of shish-kebabs in-situ is the enormous speed at which these structures propagate, in the order of micrometers per second [22]. Conventionally the acquisition time of X-Ray scattering images, the most likely candidate for studying these phenomena, is too high to resolve shish growth. Consequently, the growth mechanism is still shrouded in clouds.

Recent technical improvements at the BM26 beamline at the European Synchrotron Radiation Facility have enabled WAXD acquisition with 30 Hz. In this paper, we study the mechanism behind shish growth by subjecting a polymer melt to flow in a slit at high wall shear rates (up to \(\sim 900 \text{s}^{-1}\)), combined with this in-situ X-Ray Diffraction technique. The flow was ceased at various times to allow characterization of structural development afterwards by taking "snapshots" at different development stages of shish. A detailed picture of the growth of shish-kebabs results.

6.2 Experimental

We conducted experiments on an iPP homopolymer (Borealis HD601CF, \(M_w = 365 \text{ kg} \cdot \text{mol}^{-1}\), \(M_n = 68 \text{ kg} \cdot \text{mol}^{-1}\)) also examined in other crystallization studies [16, 168]. Flow is applied in a confined slit flow geometry within a modified Multi-Pass Rheometer, by simultaneously moving the two pistons between which the material is confined in the same direction. This setup allows for simultaneous probing of rheology, via pressure transducers positioned near both pistons, and structure development, through windows in the slit placed halfway between both pistons. Detailed and full description of similar, earlier experiments are provided elsewhere [44]. Samples were molten at 220 °C for 10 minutes to erase thermo-mechanical history. Hereafter, the samples were cooled to a temperature of 145°C and subjected to flow at different piston speeds for different flow durations, see Table 6.1.

\(^1\) more accurately; a precursor formed by flow which, if flow was ceased at an earlier time, would be so far away from other nuclei that it would be entirely covered by spherulitic overgrowth [167]
Table 6.1: Experimental conditions in the MPR. Wall shear rate $\dot{\gamma}_w$ and wall shear stress $\sigma_w$ were calculated at steady state using a Carreau-Yasuda model for the shear rate dependence of the viscosity.

<table>
<thead>
<tr>
<th>Piston speed [mm/s]</th>
<th>Flow duration [s]</th>
<th>$\dot{\gamma}_w$ [s$^{-1}$]</th>
<th>$\sigma_w$ [x 10$^5$ Pa]</th>
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<tr>
<td>60</td>
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<td>370</td>
<td>1.21</td>
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<td>80</td>
<td>0.25</td>
<td>500</td>
<td>1.35</td>
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<tr>
<td>100</td>
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<td>635</td>
<td>1.47</td>
</tr>
<tr>
<td>120</td>
<td>0.11-0.17-0.20-0.23</td>
<td>769</td>
<td>1.57</td>
</tr>
<tr>
<td>140</td>
<td>0.20</td>
<td>904</td>
<td>16.6</td>
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</tbody>
</table>

Morphological and structural development were evaluated during flow and during subsequent isothermal crystallization using wide-angle X-ray diffraction (wavelength $\lambda = 1.033$ Å) at the beamline BM26B [169] of the ESRF (Grenoble, France). During and immediately after flow, 2D patterns were recorded at a frequency of 30 Hz for a total time of 2 seconds using a Pilatus 300K detector. Subsequent isothermal crystallization was monitored in a higher azimuthal range (> 90°) using a Frelon detector with an acquisition time of 2.66 seconds per frame and a total duration of 22 minutes.

Crystallinity was calculated from the radially integrated patterns as the ratio between the scattered intensity by crystals and the total scatter intensity. For the data collected with the Pilatus, the area of the reflection is given by the area underneath the (isotropic) baseline subtracted scattering pattern. Regarding the patterns acquired with the Frelon detector, azimuthal scans of the (110) reflection were fitted by Lorentzian peaks, which were integrated to obtain the area of the peaks. Proper geometrical corrections were applied [159]. Examples of procedures for both detectors are given in Fig. 6.1.

Figure 6.1: Azimuthal scans of the (110) diffraction of WAXD patterns (inserted) obtained with (a) Pilatus detector and (b) Frelon detector. Flow direction is vertical.
6.3 Results

The pressure drop signal for all experiments is presented in Fig. 6.2. Reproducibility is observed to be excellent. Steady state is reached after 0.08 s for 120 mm/s piston speed and 0.1 s for 100 mm/s. For high piston speeds, the pressure drop starts to increase at some point due to structure formation in the high shear rate regions near the walls, effectively decreasing the thickness of the channel while the volumetric flow rate prescribed by the pistons remains the same. After stopping the flow, the pressure relaxes quite rapidly, indicating that the majority of crystal growth happens at near atmospheric pressure.

![Figure 6.2: Pressure drop between the pistons for all piston speeds and flow times](image)

The apparent crystallinity (apparent, as it is an average crystallinity over the slit, because the beam traverses across velocity gradient direction) is shown for all shear times in figure 6.3(a). Time $t = 0$ is the start of flow. As expected, a longer flow time results in a higher amount of crystalline structure and hence in a higher apparent crystallinity. For all flow conditions, we observe the characteristic S-shaped curve indicative of crystallization until impingement, which seems to occur around 100 s (this is also the expected time for impingement with inter-shish distance of $\sim$100-200 nm (Fig. 6.4 and ref. [112]) and crystal growth rate of $\sim$4 nm/s [151]). We conclude that the first 100 s show the crystallization of the shear layer near the walls with dense highly oriented crystalline structures. After impingement, apparent crystallinity continues to increase at a lower slope. For all experiments the increase in apparent crystallinity between 100 s and 1200 s is 8%. This is ascribed to crystallization in the fine-grained layer with isotropic structures [3], or perhaps less densely packed shish, known as sausages [22].

Because the shear layer has fully crystallized after 100 s, and crystallinity in the fine-grained layer is still negligible at this time, the space filling within the shear layer can be quantified by normalizing the apparent crystallinity with the value at $t = 100$ s. Doing so, we obtain figure 6.3(b). Surprisingly, the data overlap perfectly for all flow conditions for $t \geq 3$ s. Hence, although the thickness of the shear layer is too thin to give a signal in the frames with the short acquisition time.

\[^{2}\text{For the measurement with piston speed 60 mm/s, the shear layer is too thin to give a signal in the frames with the short acquisition time.}\]
shear layer grows with shear time, the crystallization kinetics within the layer are unaffected by flow rate or time. Only at short times \( t < 3 \) s there is an observable difference; for faster piston speeds the shear layer is formed more quickly. At longer times this time delay becomes negligible. Because crystallization kinetics are a direct result of the crystalline structure, this implies that the crystalline structure is also identical for all flow conditions.

To verify this observation, we performed TEM on a sample obtained at the strongest flow condition (140 mm/s for 0.2 s). The sample was prepared and analyzed in the same way as in ref. [168]. Figure 6.4 shows pictures obtained within the shear layer at two locations separated by 350 \( \mu \)m in velocity gradient direction. Indeed the morphology in both pictures looks very similar. This is also shown by the Fourier Transforms of the TEM pictures (inserted). The positions of the lobes on the equator relate to long spacing of the kebabs and the streaks on the meridian indicate the distance between shish. These show no observable difference between the two positions where TEM pictures were taken. Hence these results confirm that crystalline morphology within the shear layer does not depend on position.

The Kornfield group already observed indications for the saturation of shish density, albeit at a somewhat milder flow condition and longer shear times (65kPa for 7 s and 12 s [31] and 60 kPa for shear times above 4 s [23]). Especially the pictures in ref. [23] clearly show the phenomenon. They came to the hypothesis that structure formation influences the rheology of the material, increasing resistance to deformation, which at a certain point stops further growth of shish and therefore results in a saturation of shish density. The capability of our set-up to simultaneously measure rheology and WAXD enables a detailed study behind the physics of this surprising phenomenon. Indeed, the growth of the shear layer to considerable proportions coincides with an increasing pressure drop. This observation supports the hypothesis that changing rheology is halting shish growth.

The question arises what the exact cause of the viscosity upturn is. The possibility of a percolating network formed by chains connecting shish is excluded; the radius of gyration of PP can be estimated by \( R_g/M_w^{1/2} = 0.039 \) nm [170], giving an average of \( R_g = 23.5 \) nm for the material in this study, while shish are typically 100-200 nm apart (Fig. 6.4 and ref. [112]). Hence, a chain with average length will probably not form a link between shish. For our material, which is quite polydisperse, one
could imagine that some chains on the high end of the molecular weight distribution are in fact long enough, but the material in the work from the Kornfield group [31] is much less polydisperse. If the physics behind saturation of shish density in these experiments are the same, a percolating network can not be the cause of the viscosity upturn.

Instead, the Kornfield group proposed that space filling of kebabs was such that the suspension of shish-kebabs was altering the rheology of the material. We can easily estimate if the proposed effect can be strong enough. Take $t = 0.2$ s. The measurements with a piston speed of 120 mm/s give a pressure drop of 550 bar; an increase of a factor 1.5 with respect to the steady state value at 0.1 s. Hence, on average, all the material in the entire slit has a viscosity of 1.5 times the viscosity of the melt. The space filling in the shear layer in the middle of the slit at this point in time is 5% (Fig. 6.3(b)). We can estimate that such a volume fraction of perfectly aligned fibers would increase the modulus of iPP by a factor of $1.10^3$.

Based on the observations and the approximated quantification of the different effects, we can conclude that purely a suspension of shish would not affect the viscosity of the melt enough to explain the pressure drop observed.
Instead shish-kebabs must affect the melt rheology in a different way. We propose the following: some chains are partially inside the shish and partially inside the melt. Keller dubbed these chains "hairs" [164, 171], and hypothesized these crystallize subsequent to shish, forming the kebabs. We propose that these hairs interact with the surrounding melt and as a consequence cause a greater disturbance in the flow field around the shish than would have been the case if the shish were smooth.

The following conceptual model is proposed to explain the experimental observations presented in this paper. Figure 6.5 serves as illustration, showing in the top row a schematic depiction of the morphology at a point somewhere along flow direction and in the bottom row shear stress and shear rate as a function of position along thickness direction. Time increases from left to right. Shortly after the start of flow, a flow field develops with high shear rate near the walls and zero shear rate in the center of the slit (Fig. 6.5(a)). As a result, flow-induced nuclei appear; near the wall a large density appears which quickly falls off going from the wall to the center of the slit. Near the wall, stretched chain segments attach to the existing nuclei forming shish (b). As material is continuously sheared, shish grow in length, increasing their volume fraction and, more importantly, increasing the total number of "hairs" that interact with the surrounding melt. At a certain point, their number becomes that large that the overall rheology of the material is macroscopically affected, causing a decrease in the deformation rate in the layer near the wall and an increase in the overall pressure drop (c). Because the deformation rate in the shear layer decreases, shish stop growing. Instead, because the total volumetric flow rate remains constant, the shear rate experienced by the material just outside the shear layer increases, causing the formation of shish (d) until the point where the increase in modulus hinders further shish growth (e-f), at which point the shear layer grows even thicker. This sequence of events continues until flow is ceased. Effectively, there is a front of shish-kebabs that propagates towards the center, with a layer with high density of point-like nuclei with constant density in front.

The Generalized Self Consistent Method gives the following expression for the modulus of a suspension of perfectly aligned fibers with concentration $c$:

$$
\frac{G(c)}{G_m} = \frac{G_f(1 + c) + G_m(1 - c)}{G_f(1 - c) + G_m(1 + c)}
$$

with $G_m$, $G_m$, $G$ the moduli of the matrix, the fibers, and the suspension in the direction in which the fibers are aligned, respectively. For a volume fraction of 5%, this yields $G/G_m = 1.10$ with $G_m = 10^4$ Pa and $G_f = 10^8$ Pa for iPP [16]. To get $G/G_m = 1.5$, we need $c = 0.2$. Alternatively, we might compare shish-kebabs to glass fibers, which are also much stiffer than the melt and typically have aspect ratios in the order of 100. Experimental data for such systems also show that volume fractions exceeding 10% are needed to give a viscosity increase of factor 1.5 [172–176].

It takes the material near the windows 4 seconds to reach a space filling of 20%. Material upstream experiences faster structure formation, but this difference is not expected to be big enough to explain the pressure drop increase purely from a suspension of shish. The start-up time of the flow is ~0.1 s, hence we can expect a time delay in flow history ~0.05 s between material upstream and in the middle of the slit. Moreover, the pressure drop is ~350 bar during the early stage of structure formation, giving a pressure difference between upstream and the middle of the slit of ~175 bar, amounting to a depression in melting point of about 5°C [177]. Neither of these effects are strong enough to accelerate crystallization enough to result in a space filling of 20% upstream already at 0.2 s.
6.4 Conclusion

In conclusion, we have shown that the shish density within the shear layer formed in a slit flow geometry is independent on shear rate and shear time. A conceptual model is proposed to explain this observation, with the key ingredient that chains protruding from shish into the amorphous melt disturb the flow field around shishes. These macroscopically increase the modulus of the material and thus, at a certain density of shish, hinder further deformation and stop shish growth. Because volumetric flow rate remains constant, the material just outside the shear layer then experiences larger shear rates, causing shish to appear and the thickness of the shear layer to increase.

Acknowledgements

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Chapter 7

Numerical simulation of flow-induced crystallization in isotactic polypropylene at high shear rates

Abstract

In this chapter a model is developed and validated to quantify the self-regulating effect that was experimentally observed in chapter 6. A 2D finite element code is developed to simulate the experiments in terms of velocity field, pressure, temperature, and crystalline morphology. The model accounts for effects of viscoelasticity, compressibility, and varying temperature due to shear heating. Following Chapter 3, flow-induced nucleation takes place with a rate coupled to backbone stretch in the longest mode, obtained from the viscoelastic constitutive model. Flow-induced nuclei propagate in flow direction with a speed related to shear rate, thus forming shish, which increase the viscosity of the material. The viscosity change with shish formation is implemented in a phenomenological manner; shish act as a suspension of fibers with radius equal to the distance at which the hairs of shish interact with the melt.

The model is thoroughly validated with experimental data. Quantitative agreement is observed in terms of pressure drop, apparent crystallinity, parent/daughter ratio, and shear layer thickness. Moreover, simulations for lower flow rates are performed and the results are compared, in a qualitative sense, to experiments from literature.

7.1 Introduction

Flow-induced crystallization (FIC) during processing of semi-crystalline polymers determines to a great extent the final product properties (cf. refs [2, 109, 178]). Especially at relatively low temperatures, i.e. between the melting point of crystals as measured during heating, and the crystallization temperature measured upon cooling, flow increases the number of nucleation sites. This effect increases the temperature of solidification and results in fine structures in the product's morphology. If the flow is strong enough, it can even create anisotropic crystalline structures, known as shish-kebabs. These structures, consisting of a fibrous backbone with lamellar overgrowth, were first recognized in notably stirred undercooled solutions [155, 156], and later also in polymer melts [154].

The formation of these structures has a big influence on the morphology of injection-molded products [109, 178]. Typically, going from the wall to the center of the product, one encounters first a quenched layer due to rapid cooling at the cold wall, then a highly oriented layer with shish-kebabs, followed by a fine-grained layer with a high nucleation density and finally a core with large spherulites [179]. The formation of the shear layer is commonly studied in isothermal channel flow experiments, with a combination of birefringence, X-Ray Diffraction, and ex-situ microscopy [3, 22, 25, 44, 112].

A number of models have been developed in attempts to capture the formation of shish-kebabs and the resulting shear layer. Liedauer et al. coupled the parameter $\gamma t_s^2$, with $\gamma$ the shear rate and $t_s$ flow time, to the density of shish [3, 52]. Their approach was used as a starting point for the group in Eindhoven, who linked nucleation rate to deformation of a high-molecular weight mode on a continuum level [5, 10, 46] and subsequent shish growth, after overcoming a critical flow criterion, to deformation of a mode corresponding to the average molecular weight [46, 47, 49]. This approach was validated in terms of shear layer thickness in both channel flow and a capillary rheometer. The model was also validated to be accurate in terms of crystallization kinetics in extended dilatometry experiments [50].

Recent experiments using piston driven channel flow have revealed a strong coupling between structure formation and rheology (see Chapter 6 of this Thesis and ref. [44]). As a result of this self-regulating effect, the density of shish within the shear layer is independent of flow condition, for strong enough flows. The only affected parameter is the shear layer thickness.

In this chapter, we present a model that captures all involved physics to explain these observations. The creation rate of flow-induced nuclei is governed by stretch in the high-molecular weight tail, as in previous experiments from the Eindhoven group. The shish growth mechanism is based on the "streamers" concept proposed by the Kornfield group [22], and shish growth rate is taken to be directly proportional to shear rate. It is hypothesized that shish influence the rheology in their surroundings on a scale much larger than their radius. The model is extensively validated with experiments from a channel flow, in terms of pressure drop, crystallinity, and shear layer thickness.

7.2 Experimental

Experiments were conducted using an iPP homopolymer (Borealis HD601CF, $M_w = 365$ kg·mol$^{-1}$, $M_n = 68$ kg·mol$^{-1}$) also examined in other crystallization studies [16, 168]. Flow is applied in a confined slit flow geometry within a modified Multi-Pass Rheometer, by simultaneously moving the two pistons between which the material is confined in the same direction. This setup allows for simultaneous probing of rheology, via pressure transducers positioned near both pistons, and structure development, through windows in the slit placed halfway between both pistons. Part of the experimental data used for validation purposes was already presented elsewhere [44]. The reader
is referred to this paper for a full description of the experimental setup. Samples were molten at 220 °C for 10 minutes to erase thermo-mechanical history. Hereafter, the samples were cooled to a temperature of 145°C and subjected to flow at different piston speeds for different flow durations, see Table 7.1.

Table 7.1: Experimental conditions in the MPR. Wall shear rate $\dot{\gamma}_w$ and wall shear stress $\sigma_w$ were calculated at steady state using a Carreau-Yasuda model for the shear rate dependence of the viscosity.

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<td>0.11-0.20-0.23-0.25</td>
<td>635</td>
<td>0.147</td>
</tr>
<tr>
<td>120</td>
<td>0.11-0.17-0.20-0.23</td>
<td>769</td>
<td>0.157</td>
</tr>
<tr>
<td>140</td>
<td>0.20</td>
<td>904</td>
<td>0.166</td>
</tr>
</tbody>
</table>

Morphological and structural development were evaluated during flow and during subsequent isothermal crystallization using wide-angle X-ray diffraction (wavelength $\lambda = 1.033$ Å) at the beamline BM26B [169] of the ESRF (Grenoble, France). During and immediately after flow, 2D patterns were recorded at a frequency of 30 Hz for a total time of 2 seconds using a Pilatus 300K detector. Subsequent isothermal crystallization was monitored in a higher azimuthal range (> 90°) using a Frelon detector with an acquisition time of 2.66 seconds per frame and a total duration of 22 minutes.

Crystallinity was calculated from the radially integrated patterns as the ratio between the scattered intensity by crystals and the total scatter intensity. For the data collected with the Pilatus, the area of the reflection is given by the area underneath the (isotropic) baseline subtracted scattering pattern. Regarding the patterns acquired with the Frelon detector, azimuthal scans of the (110) reflection were fitted by Lorentzian peaks, which were integrated to obtain the area of the peaks. Proper geometrical corrections were applied [159]. Examples of procedures for both detectors are given in Fig. 7.1.

![Figure 7.1: Azimuthal scans of the (110) diffraction of WAXD patterns (inserted) obtained with (a) Pilatus detector and (b) Frelon detector. Flow direction is vertical.](image)
7.3 Model

The model presented in this section is solved numerically in two dimensions with an in-house Finite Element Method (FEM) code. The mesh moves with the material, but since compressibility plays a role the density of the material is not constant. Therefore the Arbitrary Lagrangian Eulerian (ALE) formulation [180] is employed. The governing equations are solved sequentially per time step with explicit Euler time stepping, with a semi-implicit formulation of the stress in the momentum balance [181]. A number of stabilization techniques were implemented; Discrete Elastic-Viscoelastic Stress Split (DEVSS) [182, 183], Streamline-Upwind Petrov Galerkin (SUPG) [184], and log-conformation representation (LCR) [185].

7.3.1 Geometry

Figure 7.2 schematically shows the domain on which the governing equations are solved, corresponding to half of the slit in which the experiments were conducted. The thickness of the slit in velocity gradient direction $d = 1.5$ mm, the length between the two pistons $L \approx 185$ mm. The polymer melt is confined between two pistons (area $\Gamma_1 - \Gamma_2 - \Gamma_3 - \Gamma_4$). By simultaneously moving the pistons in the same direction, the material is subjected to a Poiseuille flow. Near both pistons, pressure transducers are embedded in the steel of the barrels. The distance between the two pressure transducers is 160 mm. To avoid structure formation influencing the pressure measurements, the barrels are kept at 220 °C. The barrels and the measurement geometry (which is kept at 145 °C), are separated by ceramic rings. Thermocouples are embedded in the steel at a distance from the wall of the flow geometry of $d_{\text{thermocouple}} = 0.5$ mm in the steel. The information from these thermocouples is used for the boundary condition on the temperature problem, i.e. $T = 220$ °C on $\Gamma_7 - \Gamma_9 - \Gamma_8$, and $T = 145$ °C on $\Gamma_6$.

![Figure 7.2: Geometry of the MPR. The graph indicates the initial condition for the temperature.](image-url)
7.3.2 Momentum balance

The momentum balance is given by

$$\rho(p) \left( \frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} \right) = -\nabla p + \nabla \cdot \mathbf{\tau} + \nabla \cdot (2\eta_s \mathbf{D}).$$

(7.1)

Where $\mathbf{u}$ is velocity and $\rho$ is the density of the material which depends on pressure $p$ according to Eq. 7.5. A viscous component with viscosity $\eta_s = 10^{-2}$ Pa·s is added for numerical reasons. The deformation rate tensor is denoted by $\mathbf{D}$. The extra stress is given by

$$\mathbf{\tau} = \sum_i G_i (\mathbf{c}_i - 1),$$

(7.2)

with $\mathbf{c}_i$ the conformation tensor of mode $i$, calculated with the eXtended Pom-Pom viscoelastic model [186] (see section 7.3.3).

Boundary and initial conditions

The fluid is at rest at the start of the simulation ($t = 0$),

- $\mathbf{u} = 0 \forall \mathbf{x}$.

On the driving piston, the velocity is prescribed,

- $u_x = v_{\text{piston}}$, on $\Gamma_1$,
- $u_y = 0$, on $\Gamma_1$.

On the centerline we have

- $\frac{\partial u}{\partial y} = 0$, on $\Gamma_2$,

and on the wall,

- $\mathbf{u} = 0$, on $\Gamma_4$.

On the wall near the pistons a small slip velocity is applied in $x$-direction to avoid singularities at points where the pistons and the wall meet. At the co-moving piston we define a zero force constraint,

- $\mathbf{F} = 0$, on $\Gamma_3$.

Hence the material does not stick to the co-moving piston (which would result in pressure smaller than 0). Instead, the material at this end of the channel has a straight free surface. The velocity of this free surface becomes an extra unknown, which in steady state values is equal to the velocity of the driving piston but grows to this steady state with a time scale governed by compressibility effects.

7.3.3 Constitutive Modeling

Viscoelastic fluid model

The rheological behavior of the material is modeled using the multi-mode eXtended Pom-Pom (XPP) model. This model was originally developed for branched polymer melts, but later was found to also
accurately describe the behavior of linear polydisperse melts \cite{130, 186}. The conformation tensor is given by
\[
\nabla c_i + 2 \exp \left[ \nu_i \left( \frac{\sqrt{\text{tr} c_i}}{3} - 1 \right) \right] \left( 1 - \frac{3}{\text{tr} c_i} \right) c_i + \frac{1}{\lambda_{s,i}} \left( \frac{3c_i}{\text{tr} c_i} - 1 \right) = 0. \tag{7.3}
\]
Where \( \nabla c_i \) denotes the upper convected derivative of the conformation tensor of mode \( i \), \( \lambda_{b,i} \) denotes the relaxation time for backbone tube orientation of mode \( i \), \( \lambda_{s,i} \) denotes backbone stretch relaxation time of mode \( i \) and the parameter \( \nu_i \) depends on the number of arms of the molecule \( q_i \) following \( \nu_i = 0.1/q_i \) \cite{130}. The backbone stretch, used in the crystallization model to calculate nucleation density, is given by
\[
\Lambda_i = \sqrt{\left( \frac{\text{tr} c_i}{3} \right)}.
\tag{7.4}
\]

The linear viscoelastic spectrum of the iPP used in this study, obtained from small angle oscillatory shear (SAOS) measurements, is given in table 7.2. The stretch relaxation times (needed to calculate backbone stretch in the XPP model) are somewhat more difficult to determine, as this material hardly shows strain hardening in the range of strain rates that can be probed by the usual experimental techniques \cite{5, 116}. The relation \( \lambda_{s,i} \approx \lambda_{b,i}/4 \) has been observed for several other polydisperse linear polymer melts \cite{130}. Therefore, we take \( \lambda_{s,i} \approx \lambda_{b,i}/4 \) for all modes but the longest, and \( q = 1 \). For the longest mode, the parameters were obtained from a fit to uniaxial extensional viscosity data \cite{116}. There is some ambiguity in the way these relaxation times are determined. However, the approach is phenomenological and some uncertainty is permitted because of the scaling parameters that link structure formation to these rheological variables. All relevant rheological parameters for the average and long modes are given in table 7.2. To capture steady state pressure drop values it was necessary to add an additional mode with low relaxation time, the viscosity of which was chosen such that steady state pressure drop values for the lowest piston speeds were in acceptable agreement with experiments. This is justified because SAOS does not probe the material at shear rates in excess of 1000 s\(^{-1}\), even with the use of time-temperature superposition. Pressure dependence of relaxation times is not implemented. Although at relevant pressures this effect is appreciable (200 bar gives an increase of a factor 1.38 in relaxation times \cite{50}), start-up behavior would not be affected because it is dominated by compressibility effects. The only significant effect would be a vertical shift in pressure drop. Hence, to get good agreement with experiments the viscosity of the shortest mode would be lower, but the overall results would not be affected. Relaxation times shift with temperature according to an Arrhenius relation with activation energy \( E_a = 40 \) kJ/mol.

<table>
<thead>
<tr>
<th>Mode</th>
<th>Viscosity ( \eta_{0,i} ) [Pa·s]</th>
<th>Backbone tube relaxation time ( \lambda_{b,i} ) [s]</th>
<th>Backbone stretch relaxation time ( \lambda_{s,i} ) [s]</th>
<th>Number of arms ( q_i ) [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20.0</td>
<td>5 \cdot 10^{-5}</td>
<td>2 \cdot 10^{-4}</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>131</td>
<td>0.0014</td>
<td>3.5 \cdot 10^{-4}</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>303</td>
<td>0.011</td>
<td>2.7 \cdot 10^{-3}</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>480</td>
<td>0.060</td>
<td>1.5 \cdot 10^{-2}</td>
<td>1</td>
</tr>
<tr>
<td>5</td>
<td>377</td>
<td>0.29</td>
<td>7.3 \cdot 10^{-2}</td>
<td>1</td>
</tr>
<tr>
<td>6</td>
<td>183</td>
<td>1.67</td>
<td>0.42</td>
<td>1</td>
</tr>
<tr>
<td>7</td>
<td>46.0</td>
<td>11.5</td>
<td>2.21</td>
<td>12</td>
</tr>
</tbody>
</table>

Table 7.2: Linear viscoelastic spectrum at \( T_{\text{ref}} = 220 \) °C.
Compressibility

The compressibility of the material is taken into account by considering the polymer melt like an elastic solid in volume,

$$ p = p_0 - K \ln J. $$

(7.5)

Where \( p \) is pressure, \( p_0 \) is initial pressure, \( K \) is compression modulus and the Jacobian \( J = \det F \) with \( F \) the deformation gradient tensor between the initial (reference) configuration \( \Omega_0 \) and the current configuration \( \Omega \). The Jacobian \( J \) is a measure for the change in volume. For iPP, the compressibility modulus \( K = 10^9 \text{ Pa} \) \[187, 188\].

7.3.4 Heat balance

The crystallization process, both in terms of structure formation and crystal growth, is strongly dependent on temperature. To calculate the temperature, the heat balance is solved,

$$ \rho_k c_{p,k} \frac{DT}{Dt} = \lambda_p \kappa \nabla^2 T + \rho_k c_{\infty} \Delta H \frac{d\xi}{dt} + \sigma \cdot \mathbf{D}, $$

(7.6)

where \( \frac{DT}{Dt} = \frac{\partial T}{\partial t} + \mathbf{u} \cdot \nabla T \). Subscript \( k \) denotes polymer or steel. Values of parameters are given in Table 7.3. The first term in the right hand side represents heat conduction, the second term latent heat release due to crystallization (Eq. 7.23), and the third term shear heating, with stress calculated from the XPP model (Eq. 7.3). We do not take into account the changes of specific heat, thermal diffusivity, and density with temperature or during the phase transition from the molten to the crystalline phase. Because most of the heat is generated by shear heating during flow, while all the polymer is in the molten phase, we expect these effects to be minor. Moreover, the anisotropy of the thermal diffusivity, which can be significantly increased in the direction of flow\[189\], is not accounted for. Because the thermal gradient in flow direction in our experiments is generally quite small and the thermal diffusivity perpendicular to flow direction is affected much less \[189\], we trust this is a reasonable approximation.

<table>
<thead>
<tr>
<th>Table 7.3: Material parameters for the heat balance</th>
</tr>
</thead>
<tbody>
<tr>
<td>parameter</td>
</tr>
<tr>
<td>density (polymer)</td>
</tr>
<tr>
<td>heat capacity (polymer)</td>
</tr>
<tr>
<td>heat conduction coefficient (polymer)</td>
</tr>
<tr>
<td>final crystallinity</td>
</tr>
<tr>
<td>heat of crystallization</td>
</tr>
<tr>
<td>density (steel)</td>
</tr>
<tr>
<td>heat capacity (steel)</td>
</tr>
<tr>
<td>heat conduction coefficient (steel)</td>
</tr>
</tbody>
</table>

Boundary and initial conditions

The initial condition for the temperature is shown in Fig. 7.2; in both barrels, the temperature is 220 °C with a gradient over the ceramic rings. In the flow geometry the temperature is 145 °C. For boundary conditions, we prescribe the temperature of the barrel on both pistons,
• $T = 220 \, ^\circ C$ on $\Gamma_4 - \Gamma_9$ and on $\Gamma_2 - \Gamma_8$.

On the centerline, we have

• $\frac{\partial T}{\partial y} = 0$, on $\Gamma_2$.

And on the horizontal line coinciding with the thermocouples, we prescribe

• $T = 220 \, ^\circ C$ on $\Gamma_5$, $\Gamma_7$,
• $T = 145 \, ^\circ C$ on $\Gamma_6$.

• The temperature varies linearly in position from $220 \, ^\circ C$ to $145 \, ^\circ C$ on the ceramic rings.

### 7.3.5 Structure formation

Extensive research in the past decade into the phenomenon of flow-induced crystallization has indicated that flow-enhanced point-like nucleation is dominated by the chains on the high end of the molecular weight distribution [5, 10, 111]. Similar to the approach taken in refs. [5, 10, 49, 168], the creation rate of point-like nuclei is coupled in a phenomenological way to the momentary stretch in the high molecular weight tail of the material (corresponding to the longest mode in Table 7.2) on a continuum level,

$$\partial_t N_f = g_n(T, p) \exp \left( \mu_n (\Lambda_{hmw}^2 - 1) \right). \tag{7.7}$$

where $\Lambda_{hmw}$ is the backbone stretch calculated using the eXtended Pom-Pom constitutive model [130], and $\mu_n$ and $g_n$ are scaling parameters, the latter of which depends on temperature and pressure following

$$g_n(T, p) = g_{n,ref} 10^{c_{n,T}(T-T_{ref})+c_{n,p}(p-p_{ref})} \tag{7.8}$$

All parameters in the above equations are given in table 7.4. The characterization of this model is elaborated on in section 7.A.

<table>
<thead>
<tr>
<th>parameter</th>
<th>value</th>
<th>unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$g_{n,ref}$</td>
<td>$10^{12}$</td>
<td>$\text{m}^{-3} \text{s}^{-1}$</td>
</tr>
<tr>
<td>$c_{n,T}$</td>
<td>-0.0016</td>
<td>$^\circ \text{C}^{-1}$</td>
</tr>
<tr>
<td>$c_{n,p}$</td>
<td>$7.58 \cdot 10^{-4}$</td>
<td>$\text{bar}^{-1}$</td>
</tr>
<tr>
<td>$\mu_N$</td>
<td>0.0030</td>
<td>[-]</td>
</tr>
</tbody>
</table>

Table 7.4: Parameters for the flow-induced nucleation model at reference temperature of $166 \, ^\circ C$ and reference pressure of 100 bar

The growth mechanism in our model (see Fig. 7.3) is based on the "streamers" concept proposed by the Kornfield group [22]. Shish propagate in lengthwise direction by the addition of chain segments with length $\xi_{seg}$. In a crude sense, the flow attaches these segments as crystals to the tip of the shish. Because deformation rates in the channel are high (possibly even more so in the surroundings of a shish [190]), we can assume that the material deforms affinely. We can then express the lengthwise propagation speed of a shish as

$$\dot{L} = \dot{\xi}_{seg}. \tag{7.9}$$
In our model, all nucleation sites grow in lengthwise direction with this mechanism. Therefore, the total line nucleation density for kebabs, i.e. the specific shish length, is given by

\[ \partial_t L_{tot} = 2N_f \gamma \xi_{seg}. \]  

(7.10)

Note that there is not a critical flow condition for the formation of shish. However, for weak to mild flow conditions, no shish creation is observed, because nucleation rate \( \partial_t N_f \) as well as propagation rate \( \partial_t L \) are low for such flow conditions. There is no explicit dependence on molecular weight in the growth rate of shish; this comes in via the nucleation rate \( \partial_t N_f \), which is coupled to backbone stretch in the high-molecular weight tail.

Figure 7.3: Schematic depiction of segment addition to a shish.

In Chapter 6 it was observed that shish strongly influence the rheology of the melt before the crystalline volume fraction reaches considerable proportions. Chains protruding from the shish into the melt, so-called "hairs" [164, 171], were hypothesized to influence the rheology on a macroscopic scale. This is implemented in an empirical way. In Chapter 2, it was shown that the dynamic viscosity as a function of space filling is accurately described by the simple equation

\[ \log_{10} \left( \frac{|\eta^*| (\xi, \omega)}{|\eta^*| (\xi = 0, \omega)} \right) = \log_{10} (\mu, \omega) \xi, \]  

(7.11)

where

\[ \mu(\omega) = \frac{|\eta^*| (\xi = 1, \omega)}{|\eta^*| (\xi = 0, \omega)} \]  

(7.12)

is the frequency dependent ratio between the dynamic viscosity of the solidified and molten material. Obviously there are a number of limitations to this approach which restrict its suitability for the current conditions. First, the material in Chapter 2 crystallized in quiescent conditions, yielding spherulites, whereas the material will crystallize in highly oriented, more elongated structures. Second, the approach was validated only for small angle oscillatory shear, whereas in the experiments in this Chapter the material is flowing with \( \dot{\gamma} \approx 1000 \text{ s}^{-1} \). Therefore the relevant material properties are not only the linear viscoelastic properties, but also the non-linear viscoelasticity; not only the viscosity is affected, but we also expect shear-thinning behavior to be affected by this more solid-like phase [191]. Unfortunately however, at the moment we are unable to formulate a more detailed model for these complex structures. The most straightforward way of implementing the proposed effect,
require the least adjustable parameters, is to adjust the viscosity of the material via the modulus. Therefore we express the moduli of the material as [41]

\[ G_i = G_{0,i}10^{\log_{10}(\mu)v_{\text{eff}}}. \] (7.13)

Here, \( G_{0,i} \) is the modulus of mode \( i \) in the molten state as given in Table 7.2, \( \mu \) is the ratio between moduli of crystal and melt, typically for iPP \( \mu = 10^4 \) [16]. Finally, \( v_{\text{eff}} \) is the effective space filling of shish-kebabs, taking into account their hairy nature, given by

\[ v_{\text{eff}} = 1 - \exp\left(-\pi L_{\text{tot}} r_{\text{eff}}^2\right). \] (7.14)

Where \( r_{\text{eff}} \) is the effective radius of a shish. Due to the number of uncertainties in this approach, we will treat \( r_{\text{eff}} \) as an adjustable parameter. A priori, we expect \( r_{\text{eff}} \) to be in the order of 35 nm, because shish have a typical radius of 10 nm and the average radius of gyration of this material can be estimated to be 23.5 nm [170].

### 7.3.6 Crystallization kinetics

Due to the speed at which crystallization progresses in the conditions of interest, the heat released during crystallization cannot be diffused fast enough to keep the sample at constant temperature. Therefore the temperature dependence of the crystal growth rate needs to be accounted for. The growth rate in quiescent conditions can be calculated with [151]

\[ G_q = G_{\text{ref}} \exp(-c_G(T - T_{\text{ref}})^2), \] (7.15)

where \( G_q \) is the crystal growth rate in quiescent conditions, and \( G_{\text{ref}} \) and \( c_G \) are parameters given in table 7.5. The reference temperature \( T_{\text{ref}} \) depends on pressure according to the Clapeyron equation;

\[ T_{\text{ref}}(p) = T_{\text{ref}}^0 + \zeta(p - p_0). \] (7.16)

With \( p \) pressure in bar, \( p_0 \) the reference pressure of 1 bar, and \( \zeta \) the pressure dependence of the melting temperature, \( \zeta = 27.5 \, ^\circ\text{C/kbar} \) [177]. The reference temperature \( T_{\text{ref}}^0 \) is given at \( p = 1 \) bar in table 7.5.

<table>
<thead>
<tr>
<th>quantity</th>
<th>symbol</th>
<th>value [unit]</th>
</tr>
</thead>
<tbody>
<tr>
<td>maximum crystal growth rate</td>
<td>( G_{\text{ref}} )</td>
<td>4.5 [( \mu \text{m/s} )]</td>
</tr>
<tr>
<td>growth rate temperature dependence</td>
<td>( c_G )</td>
<td>0.0023 [1/K]</td>
</tr>
<tr>
<td>reference temperature</td>
<td>( T_{\text{ref}}^0 )</td>
<td>363 [K]</td>
</tr>
</tbody>
</table>

Additionally, as proposed in Chapter 5, the growth of kebabs is promoted during the flow pulse and relaxation afterwards, because chains are oriented in the c-axis direction of their unit cells [30, 42]. We account for this in an empirical way; during flow the growth rate is of parents is increased with a factor \( \mu_{\text{flow}} \). After flow this effect relaxes due to chains relaxing towards their equilibrium conformation with a timescale \( \lambda_G \). The growth rate of parent lamellae \( G_p \) is given by

\[ G_p(t, T) = G_q(T) \left[1 + \mu_{\text{flow}} \exp\left(-t/\lambda_G\right)\right], \] (7.17)

where \( \mu_{\text{flow}} \) is the additional growth rate due to flow, \( \lambda_G \) is the relevant time scale for relaxation of this effect, and \( t \) is the time since the cessation of flow. In the present experiments, we use the same values as found in Chapter 5; \( \mu_{\text{flow}} = 4 \), \( \lambda_G = 9 \) s.
The chain orientation and stretch in flow direction makes crystallization in the daughter morphology less preferable. However, because growth of daughter crystals only becomes noticeable when the chains have relaxed to their equilibrium conformations, we take the growth rate for this species always equal to the quiescent growth rate. For the isotropic spherulites we also take the growth rate equal to the value in quiescent conditions,

\[ G_d(T) = G_{sph}(T) = G_q(T). \]  

To calculate crystalline volume fraction from the nucleation density, specific shish length, and crystal growth rate, the Schneider rate equations [7, 51] are used. These equations form a set of coupled differential equations to calculate the evolution of length density, area density, and undisturbed volume fraction for spherulites from number density and crystal growth rate. These equations read

\[
\begin{align*}
\partial_t \phi_3 &= 8\pi \partial_t N \quad (\phi_3 = 8\pi N), \\
\partial_t \phi_2 &= G_{sph} \phi_3 \quad (\phi_2 = 8\pi R_{tot}), \\
\partial_t \phi_1 &= G_{sph} \phi_2 \quad (\phi_1 = S_{tot}), \\
\partial_t \phi_0 &= G_{sph} \phi_1 \quad (\phi_0 = V_{tot}),
\end{align*}
\]

where \( G_{sph} \) is the crystal growth rate as determined from Eq. 7.15. The flow-induced nucleation rate \( \partial_t N \) is given by Eq. 7.7. For the kebabs growing on shish (parents) we have

\[
\begin{align*}
\partial_t \psi_{2,p} &= 4\pi \partial_t L_{tot}, \\
\partial_t \psi_{1,p} &= G_p \psi_{2,p}, \\
\partial_t \psi_{0,p} &= G_p f_p \psi_{1,p}.
\end{align*}
\]

Here \( L_{tot} \) denotes the specific shish length given by Eq. 7.10, \( G_p \) is the crystal growth rate of parent species, and \( \psi_{2,p}, \psi_{1,p}, \) and \( \psi_{0,p} \) are measures for the shish length per unit volume, the surface area of kebabs, and undisturbed volume of kebabs, respectively. The volume fraction of the shish is neglected, because it is very small compared to the total volume of shish-kebabs (the radius of a shish is in the order of 10 nm [164] while the radius of a shish-kebab grows up to about 100 nm (cf. ref. [112] and Chapter 6 of this Thesis).

Following the model proposed in Chapter 5, daughter lamellae nucleate on the surface of the parents;

\[
\partial_t \psi_{0,d} = G_d f_d \psi_{1,p},
\]

where \( \psi_{0,d} \) is the undisturbed volume fraction of daughters. The surface area of parent crystals, \( \psi_{1,p} \), is obtained from Eq. 7.20. This area acts as nucleation site for both parents and daughters, which is allocated to either parent or daughter morphology based on their momentary growth rates;

\[
\begin{align*}
  f_p &= \frac{G_p}{G_p + G_d}, \\
  f_d &= \frac{G_d}{G_p + G_d}.
\end{align*}
\]

Here too it is important that during flow the crystallization of parent crystals is promoted: during flow, when the crystal growth rate of parents is increased with respect to the quiescent value, more surface of the kebabs is assigned to nucleate parent crystals.
To correct for impingement, we use the well-known Kolmogorov-Avrami equation \[39\];

\[\xi = 1 - \exp \left( -\phi_0 - \psi_{0,p} - \psi_{0,d} \right),\]

where \(\xi\) is the crystalline volume fraction, or space filling. From Eq. 7.23 follows that the respective crystallization rates of spherulites, parents, and daughters are given by

\[
\begin{align*}
\partial_t \xi_{\text{sph}} &= (1 - \xi) \partial_t \phi_0 \\
\partial_t \xi_p &= (1 - \xi) \partial_t \psi_{0,p} \\
\partial_t \xi_d &= (1 - \xi) \partial_t \psi_{0,d}.
\end{align*}
\]

(7.24)

When crystallization is complete, the total space filling \(\xi = \xi_{\text{sph}} + \xi_p + \xi_d = 1\). By looking at the individual contributions from the different morphologies, we can quantify the final crystalline structure in terms of morphological composition.

### 7.4 Results

In this section we present simulations with the current model. First, the significance of compressibility effects is highlighted. Second, the interplay between the velocity field, structure formation, and temperature is demonstrated. Further, we demonstrate the effect of the two adjustable parameters, the segment length \(\xi_{\text{seg}}\) and the radius at which shish influence the rheology \(r_{\text{eff}}\). Next, the current model is quantitatively validated with the experiments presented in section 7.2. We compare results from the model presented in this chapter with previous simulation work from our group \[46, 49, 50\]. Finally, results of the model in milder conditions are compared in qualitative terms with experiments from literature.

#### 7.4.1 Compressibility effects

It is important to realise that in such extreme conditions, compressibility of the polymer melt plays an important role in start-up behavior. This is illustrated by Fig. 7.4, where simulations and experiments are compared, with the only difference that in the results depicted in the left figure the material is incompressible, and compressibility is switched on for the results shown in the right figure. Clearly the dominant timescale for flow start-up is the compressibility, as was also observed in for example ref. [192]. The upturn in pressure drop for higher flow rates is caused by structure formation, which was turned off in these simulations.
Numerical simulation of FIC in iPP at high shear rates

Figure 7.4: Time evolution of pressure drop over the slit. Symbols show measurements, lines show simulations for the iPP used in this study, which is taken to be incompressible (a) or compressible (b). Signals are shifted in vertical direction for clarity.

7.4.2 Interplay between structure formation and rheology

Figure 7.5 demonstrates the evolution of several quantities during flow with a piston speed of 100 mm/s for 0.20 s. The flow start-up behavior is demonstrated in the first and fourth column, showing velocity and pressure, respectively. The temperature, shown in the right column, clearly shows strong shear heating effects; the temperature increases by as much as 5 °C.

The specific shish length is presented in the middle column. From 0.10 s, a significant part of the channel is filled with a high amount of shish (inter-shish distance of roughly 100 nm). As a result, the viscosity of the material in this region is increased, giving rise to a lower velocity, higher overall pressure drop, and a high shear rate region where shish formation takes place that propagates from the wall towards the center.
Figure 7.5: From left to right: velocity, shear rate, specific shish length, pressure, and temperature during flow at 100 mm/s. Time increases from top to bottom. The center line is located at $y = 0$ mm, the wall is at $y = 0.75$ mm. Flow direction is from left to right, the driving piston is at $x = 0$ mm and the co-moving piston is at $x \approx 185$ mm. Parameters are $r_{\text{eff}} = 50$ nm, $\xi_{\text{seg}} = 5$ nm.
7.4.3 Parameter variation

In Fig. 7.6 we present simulation results for a flow condition of 100 mm/s for 0.20 s, with varying segment length $\xi_{seg}$. The radius at which shish influence the rheology $r_{eff}$ was kept constant at 50 nm. The segment length only has a minor influence on the results. Notably, the specific shish length within the shear layer is hardly affected by the segment length. The main effect of varying $\xi_{seg}$ is the increased shear layer thickness; because shish grow at higher speeds, the modulus increases faster, causing a faster propagation of the shear layer.

![Figure 7.6: (a) Pressure drop, (b) apparent crystallinity, (c) shish length density at the window, for varying $\xi_{seg}$. The radius at which shish affect the rheology is kept constant at $r_{eff} = 50$ nm. Symbols show experimental data, lines show results from simulations.](image)

The specific shish length within the shear layer, and with it the crystallization kinetics, is dominated by the effective radius of shish. This is demonstrated in Fig. 7.7, where the radius at which shish affect rheology $r_{eff}$ was varied. For low $r_{eff}$, shish only start affecting rheology at a high density, resulting in a small shear layer with high nucleation density and fast crystallization kinetics. The apparent crystallinity however is quite low, because the shear layer is thin. For high $r_{eff}$, the modulus of the melt is already increased significantly for shish that are spaced far apart (i.e. low $L_{tot}$), causing a fast propagation of the shear layer front but a low total shish density within the layer.
Figure 7.7: (a) Pressure drop, (b) apparent crystallinity, (c) shish length density at the window, for varying $r_{\text{eff}}$. The segment length is kept constant at $\xi_{\text{seg}} = 5$ nm. Symbols show experimental data, lines show results from simulations.

From Figs. 7.6 and 7.7, we conclude that good agreement with experiments is obtained for the parameter set $\xi_{\text{seg}} = 5$ nm and $r_{\text{eff}} = 50$ nm. The segment length, being in the order of nanometers, attains a sensible magnitude. The same goes for the radius at which shish influence the velocity, being in the order of the radius of gyration (shish radius of 10 nm plus radius of gyration of 23.5 nm for this material [170] gives 33.5 nm).

However, it must be noted that no conclusions should be connected to the exact values of these parameters; the model is a very crude representation of what might be the actual physics taking place. The flow field around a shish is probably strongly distorted [190], so the macroscopic shear rate might be increased. Moreover, the approach with which the effect of shish on the rheology is calculated (Eq. 7.13) does not take the influence of shish on the non-linear viscoelastic properties into account. Most probably the shish not only increase the modulus, but also significantly decrease shear thinning behavior (like glass fibers, cf. ref. [191]). Therefore the relation that we used might underpredict the effect that shish have on the viscosity at these high shear rates. A more detailed model for the effect of shish-like structures on non-linear viscoelastic properties, possibly based on numerical calculations, is highly desirable. A possible direction for such a model can be found in ref. [20].
7.4.4 Validation with experimental results

The results from the previous section showed that good agreement with experiments at a flow condition of 100 mm/s for 0.2 s was obtained for the two adjustable parameters $r_{\text{eff}} = 50$ nm and $\xi_{\text{seg}} = 5$ nm. Using this parameter set, we performed simulations for additional flow condition. Comparison between experiments and simulations are presented in Fig. 7.8. Simulations capture the experimental data quite accurately, both in terms of pressure drop (Fig. 7.8(a)) and crystallinity (Fig. 7.8(b)). Note that for the fastest piston speed (140 mm/s), we only show calculated pressure drop up to 0.165 s. The reason for this is explained in Section 7.4.5. One clear discrepancy concerns the crystallization during flow; our simulations clearly underpredict the evolution of crystallinity at short times, indicating that the initial growth of shish-kebabs is much faster than in our model. A possible explanation is that chains protruding into the melt have an enhanced crystallization rate, an effect which is not accounted for in the current model.

In Appendix 7.B it is shown that the model shows satisfactory agreement with experimental data at much milder flow conditions.

![Figure 7.8](image)

**Figure 7.8**: Comparison between experiments (symbols) and simulations (lines) for five flow conditions; 60, 80, 100, 120, and 140 mm/s. Flow times are 0.25, 0.25, 0.2, 0.17, and 0.20 s, respectively. (a) Pressure drop, (b) Apparent crystallinity.

Figure 7.9 depicts the evolution of the parent/daughter ratio. Although the trend of increasing parent/daughter ratio with flow strength is captured well by our simulations, the exact values are generally underpredicted. This discrepancy might also be resolved by a higher crystallization rate during flow; as the growth of parent crystals is favorable over growth of daughter crystals during and shortly after flow, an increased crystallization rate would lead to an increased parent/daughter ratio.
Varying flow times with constant piston speed show similar trends, as demonstrated in Figure 7.10. The increase of shear layer thickness and parent/daughter ratio with flow time is captured by simulations. However, crystallization kinetics at short times as well as parent/daughter ratio are underpredicted for all flow conditions.

Figure 7.9: Parent/daughter ratio from experiments (symbols) and simulations (lines).

Figure 7.10: Apparent crystallinity (a) and parent/daughter ratio (b) for flows with piston speed 120 mm/s for varying flow times. Symbols indicate measurements, lines are simulations.
7.4.5 Shear layer thickness and flow instabilities

Figure 7.11 shows Polarized Optical Microscopy (POM) pictures of the sample in the slit at nine positions along flow direction, for piston speeds of 60 mm/s (a) and 140 mm/s (b). The shear layer is distinctly visible in the POM images. The specific shish length from simulations is shown next to the POM images, where the color scale ranges from inter-shish distance of 1 mm (blue) to 50 nm (red). For the piston speed of 60 mm/s, shear layer thickness is captured very accurately. For the piston speed of 140 mm/s however, we are unable to reproduce the experimental results. As the thickness of the shear layer increases and the channel effectively becomes narrower, the velocity starts showing oscillations in x-direction as a result of which the code no longer converges. The morphology that we show in Fig. 7.11 is the morphology at 0.165 s. Shortly after this moment the flow becomes unstable. The exact time at which these oscillations start occurring depends on mesh size; with a finer mesh these oscillations start at earlier times. Also, the POM images for this piston speed do not reveal the shear layers with straight edges that can be found for the lower piston speed, and also in many other studies [23, 49]. These are indications that the oscillations are not a numerical artefact, but that the flow actually might become unstable for these conditions.

Because the simulations stop converging at some time during the flow pulse, we can not quantitatively compare the shear layer thickness or crystallization kinetics for this flow condition. However, the variation of layer thickness with position along flow direction is reproduced quite well; near both pistons the shear layer is thin due to high temperature, and in between there is a negative gradient in shear layer thickness versus distance along flow direction due to pressure and start-up effects. Moreover, the pressure drop (Fig 7.8(a)) is reproduced very well up to the time where oscillations start occurring.
Figure 7.11: Polarized Optical Microscopy images side-by-side with specific shish length from simulations, where blue depicts $10^5$ m/m$^3$ and red is $10^{14}$ m/m$^3$, corresponding to a range of inter-shish distance of 1 mm to 50 nm. (a) Shows results for piston speed of 60 mm/s and flow time 0.25 s, (b) shows results for piston speed of 140 mm/s and flow time 0.165 s. The different subfigures are different positions along flow direction in the slit, from top left to bottom right: 13, 32, 53, 60, 73, 82, 90, 113, and 130 mm from the driving piston.
7.4.6 Comparison to Zuidema’s model

The approach of coupling structure formation to deformation calculated with a rheological model on continuum level was first presented by Zuidema et al. [46]. The model presented by Zuidema was slightly modified by Steenbakkers [5], who replaced the recoverable strain by backbone stretch, and also used by Custódio et al. [49]. In the aforementioned publications, shish started growing after a critical backbone stretch was reached in the high molecular weight tail. Instead, van Erp et al. showed that a more realistic critical condition is a cumulative stretch, i.e. time integral over backbone stretch[50].

The model presented in this chapter differs significantly from the aforementioned works in a number of aspects. First, in the current model the nucleation rate depends on backbone stretch of a high-molecular weight mode via an exponential relation instead of a power law. Second, there is no critical condition for the formation of shish; oriented crystals always grow and the propagation velocity is related to shear rate instead of backbone stretch of an average mode. Finally, we have added the coupling between shish formation and viscosity increase.

The reason for the first two modifications is demonstrated in Fig. 7.12, where we have shown experimental data and simulations with the current model and the most recent formulation of Zuidema’s model [50] for a flow condition of 100 mm/s for 0.2 s. It is clear that at these flow conditions, which are much stronger and shorter than the conditions at which the model was validated in previous publications, Zuidema’s model vastly underpredicts structure formation.

![Figure 7.12: Pressure drop (a) and apparent crystallinity (b) during and after flow with piston speed of 100 mm/s for 0.2 s. Symbols show experimental data, solid lines show current model, dashed lines show Zuidema’s model [50].](image-url)
Figure 7.13(a) shows the nucleation density after flow as a function of position along the slit. For Zuidema’s model, the maximum value is around $10^{14} \text{m}^{-3}$, which is what one would expect for far milder shear conditions. The nucleation density calculated by the current model is much higher. Due to the exponential relation between backbone stretch and nucleation rate, the nucleation density reaches $\approx 10^{20} \text{m}^{-3}$. The specific shish length is around $10^{13} \text{m/m}^3$ (cf. Fig. 7.6(c)); hence an individual shish has a length of around 100 nm. This is obviously much smaller than the total length of a shish, which can be in the order of micrometers. However, some authors suggest that shish consist of highly crystalline blocks connected by less ordered regions (cf. ref. [193]). This length of $\approx 100$ nm might correspond to the size of each of the crystalline blocks.

Figure 7.13(b) shows the time integral of backbone stretch of the high molecular weight mode at the wall, used as a critical condition for shish formation in ref. [50]. The critical value that van Erp et al. [50] determined was 24 s, whereas the cumulative stretch for these conditions never reaches this value.

Summarizing, Zuidema’s model is not applicable to flow conditions that are of interest in this chapter. It is for this reason that we have chosen to modify Zuidema’s model in the way presented in this Chapter. The current model also captures experimental data in milder flow conditions, as demonstrated in sections 7.4.7 and 7.B.

![Figure 7.13: (a) Nucleation density versus position along slit thickness for the current model (solid line) and Zuidema’s model (dashed line). (b) Cumulative backbone stretch in a long mode for Zuidema’s model.](image-url)
7.4.7 Structure formation at lower flow rates

The results presented in the previous sections were all obtained at high flow rates. Under these conditions, shish grow at such a speed that the specific shish length throughout the shear layer reaches the saturation level at approximately $10^{13} \text{ m/m}^3$. Outside the shear layer, no oriented crystals appear. However, experiments performed at lower flow rates by the Kornfield group, with similar material and temperature but wall shear stress in the order of $\sigma_w \approx 0.1 \text{ MPa}$ (compared to $0.12-0.17 \text{ MPa}$ for the experiments presented in this chapter), revealed qualitatively different results. For example, Fernandez-Ballester et al. found a less oriented type of morphology [22, 23], which they called "sausages". These sausages are distinctly oriented, but are further apart than shish. Furthermore, a distinct fine-grained layer (with a high nucleation density but no clear orientation) appears further inwards. In this section we demonstrate the ability of the current model to qualitatively capture these types of morphologies.

Simulations were performed for flow conditions with lower speeds and longer times compared to the simulations shown in earlier sections. The adjustable parameters are again set to $\xi_{\text{seg}} = 5 \text{ nm}$ and $r_{\text{eff}} = 50 \text{ nm}$. Figure 7.14 shows the calculated nucleation density and specific shish length after flow for 1 s and subsequent crystallization at $145^\circ \text{C}$ for 1120 s. For the lowest piston speed, the nucleation density at the wall is increased with a factor $\approx 10^5$ with respect to the quiescent value. Specific shish length however is low, $\approx 10^{10} \text{ m/m}^3$, corresponding to inter-shish distance of $\approx 10 \mu\text{m}$ [52]. Consequently, the fraction of crystal structure that is isotropic is much larger than the oriented crystal fraction (see Fig. 7.15). Note that the inner part of the material does not crystallize within the total time of the simulation due to the high temperature and low nucleation density.

![Figure 7.14: Nucleation and shish length densities for simulations with flow time of 1 s and varying piston speed.](image)

Figure 7.14: Nucleation and shish length densities for simulations with flow time of 1 s and varying piston speed.
For the flow condition with $v_{\text{piston}} = 30$ mm/s, a thin layer (thickness of 0.1 mm) with predominantly oriented structures is observed at the wall. The specific shish length density reaches values between $10^{10} - 10^{12}$ m$^{-3}$, corresponding to inter-shish distance between $\approx 750 - 7500$ nm. With such distances between shish, structures would have the space available to display noncrystallographic branching and splaying at farther distance, decreasing their degree of orientation [22]. Hence this value indicates a sausage-like structure. Outside of this layer, we again find a fine-grained layer with high nucleation density and in the middle of the slit no crystallization takes place during the time of the simulation. For the strongest flow condition, the majority of the shear layer of 0.25 mm thickness is filled with shish kebabs (inter-shish distance of $\approx 250$ nm), with a thin fine-grained layer adjacent to the shear layer.

These results demonstrate that the current model not only quantitatively captures the formation and crystallization of shish-kebab structures at high flow rates, but also qualitatively captures the formation of less oriented morphologies at lower flow rates.

![Figure 7.15: Distribution of crystal phases along slit thickness at a selected position in the slit. Piston speed increases from left to right. The corresponding steady state wall shear stresses in the absence of structure formation are respectively 0.071 MPa, 0.087 MPa, and 0.095 MPa.](image-url)
7.5 Conclusions

We have presented a detailed model for flow-induced crystallization at high shear rates. The model calculates nucleation rate from backbone stretch of a long mode. Growth of nuclei in flow direction is directly related to local shear rate. Crucially, the model describes a strong effect of shish on the macroscopic viscosity already at low volume fractions.

The model was implemented in a numerical code that solves for flow field, constitutive behavior, temperature, and crystallization kinetics in two dimensions. In this way, the model was validated with experiments at high shear rates. It was found that the model captures the necessary physics (with only two adjustable parameters) to accurately describe experimental results, in terms of morphology (i.e. shear layer thickness), crystallization kinetics, and rheology during structure formation. Simulations were also performed for milder flow conditions. It was found that qualitatively, the model predicts different types of morphology that have been observed in literature.

A recommended improvement for the current model is a more accurate description of the influence of dispersed elongated structures on viscoelastic properties at high flow rates. Furthermore, the proposed (very straightforward) relation between shear rate and shish propagation velocity needs to be more thoroughly validated, for example at different temperatures and pressures, different materials, and more complex flow fields.
7.A Characterization of flow-induced nucleation

To determine all parameters for the flow-induced nucleation model (Eq. 7.7), we used the experimental data set that was presented in refs. [50, 168]. The experiments were performed in the Pirouette extended dilatometer [50, 158, 168]; material was cooled down from the molten state at \( \sim 1 \) °C/s to room temperature in isobaric conditions at four different pressures (\( p = 100, 500, 900, 1200 \) bar). A shear pulse with a fixed duration of 1 s and varying shear rate of \( \dot{\gamma} = 0, 3, 10, 30, 100, 180 \) s\(^{-1}\) was applied at undercooling of 30 °C or 60 °C. The undercooling is the difference between the temperature where the shear pulse was applied and the melting temperature, corrected for the variation of melting temperature with pressure according to the Clapeyron equation [177]. The specific volume of the material was monitored. The experimental crystallization temperature was defined as shown in Fig. 7.16, which corresponds to a space filling of \( \sim 10\% \) [50]. The Schneider rate equations (section 7.3.6) were used to calculate crystallization kinetics during cooling. The crystallization temperature from calculations was defined at the temperature where \( \xi = 0.12 \).

![Figure 7.16: Method of determining crystallization temperature from PVT experiments.](image)

Experiments and calculations are compared in terms of dimensionless transition temperature \( \Theta \) as

\[
\Theta = \frac{T_{c \uparrow}}{T_{c \uparrow}^{Q}},
\]

with \( T_{c \uparrow}^{Q} \) the crystallization temperature in quiescent conditions and \( T_{c \uparrow} \) the crystallization temperature after shear. Hence, \( \Theta = 1 \) if shear has no effect and \( \Theta \) increases with shear rate.

Van Erp et al. determined the critical shear rate for appearance of oriented crystalline structures from SAXS [50, 168]. Generally, the morphology was isotropic for shear rates up to 100 s\(^{-1}\) and 30 s\(^{-1}\) for undercoolings of 30 °C and 60 °C, respectively. In this Appendix we use only the experiments that yielded exclusively isotropic structures to find the parameters for our flow-induced nucleation model. This model calculates nucleation rate from backbone stretch of a high molecular weight mode,

\[
\partial_t N_f = g_n(T, p) \exp \left( \mu_n \left( \Lambda_{hmw}^2 - 1 \right) \right)
\]

where the pressure and temperature dependence of \( g_n \) is given by

\[
g_n(T, p) = g_{n, ref} 10^{c_{n,T}(T-T_{ref})+c_{n,p}(p-p_{ref})}
\]

Hence, we need to determine 4 parameters to fully characterize the flow-induced nucleation; \( \mu_n, g_{n, ref}, c_{n,T}, c_{n,p} \). To achieve this the fitting is performed in three steps;
1. First, $\mu_n$ and $g_{n,\text{ref}}$ are determined from the experiments with $\Delta T = 30^\circ$C and $p = 100$ bar.

2. Second, $c_{n,T}$ is determined from the experiments with $\Delta T = 60^\circ$C and $p = 100$ bar.

3. Finally, we determined $c_{n,p}$ from the experiments with $\Delta T = 30, 60^\circ$C, and $p = 500, 900, 1200$ bar.

The resulting parameters are given in Table 7.4. The calculations with these parameters are compared with experimental data in Fig. 7.17. The experimental data and calculations show good agreement, indicating that for these conditions, the presented model gives an accurate representation of flow-induced nucleation.

Figure 7.17: Dimensionless crystallization temperature versus shear rate corrected for temperature and pressure for (a) undercooling of $30^\circ$C (i.e. $T_{\text{shear}} = 167^\circ$C at 100 bar) and (b) undercooling of $60^\circ$C (i.e. $T_{\text{shear}} = 137^\circ$C at 100 bar). Open symbols show measurements, closed symbols show calculations.
7.B Validation of shish growth model with Pirouette data

In the previous Appendix, the experimental data set obtained in the Pirouette dilatometer (at low to mild shear rates) from refs. [50, 168] was used to calibrate our flow-induced nucleation model. Based on recent experimental evidence shown in Chapter 6, in this Chapter we proposed an improved model for shish propagation, which was validated using channel flow experiments. In this Appendix we compare calculations with the improved model to experimental data at high shear rates from the Pirouette dilatometer. The same parameter set as for the channel flow experiments is used.

Figure 7.18 shows experimental data and calculations for these experiments. The black symbols indicate experiments where the final morphology was isotropic, the gray symbols indicate measurements with clear orientation. The current model shows satisfactory agreement with the experimental data in the full range of shear rates.

Figure 7.18: Dimensionless crystallization temperature versus shear rate corrected for temperature and pressure for flow at (a) undercooling of 30 °C (i.e. $T_{\text{shear}} = 167$ °C at 100 bar) and (b) undercooling of 60 °C (i.e. $T_{\text{shear}} = 137$ °C at 100 bar). Open symbols show measurements, closed symbols show calculations. Black symbols indicate isotropic final morphology (determined using SAXS), gray symbols indicate oriented final morphology. It is important to note that $\Theta$ levels off at high shear rates for $\Delta T_\gamma = 60$ °C because the crystallization temperature becomes equal to the flow temperature.
7.C Mesh and timestep convergence

Figure 7.19 depicts the evolution of pressure drop for different time step sizes. Mesh convergence is presented in Fig. 7.20. Based on these results we have performed all simulations, unless noted otherwise, with a mesh of 50x20 elements in x-y direction and a time step of $10^{-5}$ s.

![Figure 7.19: Time step convergence.](image1)

![Figure 7.20: Mesh convergence.](image2)
Chapter 8

A model for flow-enhanced nucleation based on fibrillar dormant precursors

Abstract

A model for flow-enhanced nucleation is presented based on the concept of a polymer melt containing a fixed number of nucleation precursors with a fixed size distribution. Depending on the size, precursors can either be active (i.e. susceptible to nucleation, the characteristic time scale of which is governed by the deformation rate) and grow into a spherulite or remain dormant. The size distribution of precursors is derived by combining nucleation theory and experimentally determined quiescent spherulite number densities. Longitudinal precursor growth, causing activation of dormant precursors, is a function of molecular deformation: the stretch of high molecular weight chains. Both the eXtended Pom-Pom and the Rolie-Poly model are tested to calculate the molecular deformation. A quantitative agreement is found between simulations and experimental results.

8.1 Introduction

The mechanical properties of polymer products strongly depend on processing conditions since these determine, to a great extent, the structure. For semi-crystalline polymers, flow-induced crystallization (FIC) plays a major role in this. Crystallization of polymers can be divided into three regimes;

1. Quiescent crystallization, if no flow is applied or the flow is too weak to have a significant influence on the crystallization process. Spherulitic crystalline structures (spherulites) are formed.

2. Flow-enhanced nucleation (FEN) occurs if the flow is sufficiently strong (sufficiently high deformation rate and time) to influence the nucleation kinetics. The number density of spherulites is increased.

3. Oriented precursor structures are formed if a flow that is sufficiently strong is applied for a longer period of time. As a result, oriented crystalline structures, such as shish-kebabs, are formed.

Different approaches are used to model flow-induced crystallization. Some researchers start with the classical result for homogeneous nucleation known as the Hoffman/Lauritzen expression[19, 53]. It contains the free energy as a driving force of which the entropic part is adapted by including the decrease due to the molecular orientation caused by the flow. A model using this approach was derived by Ziabicki and Alfonso, but the entropy change due to orientation alone could not reproduce effects as dramatic as observed in experiments[55]. A second approach starts from the statistical description of the evolution of the precursor size distribution in the melt [54] and, again, incorporates the effect of flow by adapting the free energy. For a model that incorporates anisotropic precursors with multiple fluctuating dimensions this leads to a rather cumbersome set of equations, containing a number of undetermined parameters (see appendix D). On the level of the precursors, a Monte-Carlo approach was used by Graham and Olmsted leading to insight on the relation between segmental orientation and the nucleation process and providing support for modeling on a continuum level[61, 62]. However, this approach is not useful on the level of process modeling, which is the final goal of this work. Based on experimental observations Eder and Janeschitz-Kriegl proposed a set of differential equations,[52] analogous to the Schneider rate equations [51] for (heterogeneous) point nucleation and subsequent spherulitical growth, that captured the observed correlations between crystalline structure measures (number and size of shish) and the applied flow. Shear rate was used as the driving force for flow enhanced nucleation and subsequent shish growth. This set of equations was the starting point for Zuidema et al. who replaced the shear rate with a measure that combines the molecular orientation and stretch of the high molecular weight tail,[46, 194] in line with experimental evidence from, among others, Vleeshouwers and Meijer[15]. With this approach they were successful in capturing the vast amount of experimental observations from the group of Eder and Janeschitz-Kriegl. This approach was extended and studied further by Custódio et al. [49, 195] and Steenbakkers and Peters[5, 118]. Finally, specific work is an often used measure to quantify the effect of flow on nucleation[4, 16, 45, 196]. However, we do not see this as a useful starting point for modeling since it does not contain any specific material parameters and, therefore, cannot serve as a tool for understanding the influence of, for example, variations in the molecular weight distribution. Rather, the outcome of our modeling should compare with the experimental results presented in terms of specific work.

The concept of dormant precursors, introduced by Janeschitz-Kriegl and co-workers, assumes that the melt contains a fixed number of precursors[45, 196]. The free energy won by crystallization
of a precursor (a volume term) competes with some kind of surface tension (a surface term). The precursors thus need to be greater than a certain critical size (denoted by \( n^* \) in this paper) for growth of a precursor to be favorable and for the precursor to become a nucleus. Precursors smaller than the critical size are defined dormant, precursors larger than the critical size are active. Active precursors may nucleate, becoming a nucleus. The terms precursors and nuclei are further clarified in figure 8.1. The figure shows a size distribution of precursors where a number of active precursors have turned into nuclei, which we consider to be the (semi-)crystalline phase and others are still present in the amorphous phase.

Figure 8.1: Size distribution of precursors where a number of active precursors have turned into nuclei. \( N_p(n) \) is the number of precursors with size \( n \) or greater, \( n^* \) is the critical size precursors need to overcome to become active. At time zero only precursors are present, as time progresses active precursors will turn into nuclei. At a sufficiently long time scale all active precursors will become nuclei.

The goal of this work is not only to model and test the idea of Janeschitz-Kriegl et al. that dormant precursors can be activated by flow, by changing (one of) the dimensions, but also to make it accessible for experimental results. For this reason we will combine classical nucleation theory, extended to two precursor dimensions, with the approach used by Zuidema et al. [46], Custódio et al. [49] and Steenbakkers and Peters[5] to derive a model for flow-enhanced nucleation based on dormant precursors.

In the "Experimental results" section we briefly summarize experiments from literature that will be used to validate our model. The derivation of the model is presented in "Theory". Simulation results and validation of the model are shown in the "Results" section. Resulting conclusions are presented in "Conclusion".
8.2 Experimental results

8.2.1 Quiescent

Predictions of the model will be compared with experiments on two grades of isotactic polypropylene (iPP). For both materials, HD601CF (previously known as HD120MO, provided by Borealis) and 13E10 (provided by DSM), the quiescent nucleus number density as a function of temperature is described by Eq. 8.1. We should note that this expression is merely an experimental fit that will give good results only in the temperature range investigated in the experiments. However, as the maximum nucleus number density that we encounter in our simulations is not vastly outside the range of the experiments described by Eq. 8.1, we expect this expression to be sufficiently accurate for current purposes. Parameters for the expression and some physical properties of the materials are shown in Table 8.1. Numbering of the materials is adopted from Housmans et al.[16].

\[ N_n = N_{ref} \exp \left( -c_N (T - T_{ref}) \right) \]  

(8.1)

The above expression yields a cumulative number density, namely that of the nuclei obtained at constant temperature \( T \) in a quiescent melt. Under these conditions, in temperature ranges of practical interest, active precursors nucleate instantaneously,[196] as evidenced by the narrow size distribution of spherulites even in systems containing very low amounts of heterogeneous substances[197, 198]. Thus \( N_n \) is equal to the cumulative number of active precursors per unit volume of the amorphous phase (their actual number in general depends on the space filling at hand, which depends on the thermal history). The differential number density \( N'_n \), is obtained by calculating the increase in spherulite number density \( \Delta N_n \) for a certain decrease of the temperature \( \Delta T \),[45] or

\[ N'_n = -\frac{\partial N_n}{\partial T} = c_N N_{ref} \exp \left( -c_N (T - T_{ref}) \right) \]  

(8.2)

From this expression the number of nuclei that will appear at a certain temperature can be obtained by integration from the experimental temperature to the nominal melting temperature. Figures 8.2(a) and 8.3(a) show both the cumulative number density \( N_n \) and differential number density \( N'_n \) for materials iPP2 and iPP3, respectively. The solid line shows Eq. 8.1, the dashed line shows Eq. 8.2. The circles show measurements of the spherulite number density obtained from optical microscopy[199, 200].

<table>
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<tr>
<th>Material</th>
<th>Grade</th>
<th>( M_w ) [kg/mol]</th>
<th>( M_w/M_n ) [-]</th>
<th>( Z = M_w/M_c ) [-]</th>
<th>Isotacticity [%]</th>
<th>( N_{ref} ) ([\text{m}^{-3}])</th>
<th>( T_{ref} ) [°C]</th>
<th>( c_N ) [°C(^{-1})]</th>
<th>refs.</th>
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<td>70</td>
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<td>1.14 ( \cdot ) 10^{14}</td>
<td>110</td>
<td>0.115</td>
<td>[16, 199]</td>
</tr>
<tr>
<td>iPP3</td>
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<td>636</td>
<td>6.9</td>
<td>122</td>
<td>94.7</td>
<td>4.05 ( \cdot ) 10^{12}</td>
<td>140</td>
<td>0.109</td>
<td>[16, 200]</td>
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</table>

8.2.2 Flow/iPP2

The first set of experiments are short-term shear experiments on iPP2, from Housmans et al[16]. Short term shear was applied in a rheometer with plate-plate configuration and the evolution of rheological properties was monitored afterwards. Table 8.2 shows the backbone tube orientation and stretch times of the slowest mode of both grades, obtained from a fit of the eXtended Pom-Pom (XPP)
model to extensional viscosity measurements. See also appendix 8.B. The spherulite number density was obtained by estimating space filling by modeling the crystallizing melt as a suspension with soft particles [20] and fitting the Avrami equation for 3D growth [39, 40] to this. More information on this procedure can be found in recent papers from Housmans et al [16] and Ma et al [9]. Figure 8.2(b) shows the nucleus number density resulting from crystallization after flow as a function of applied shear time for different shear rates. Note that the quiescent number density is a factor three smaller than Eq. 8.1 predicts with the value for $N_{ref}$ from Housmans et al. Therefore we have used an adjusted value $N_{ref} = 1.14 \cdot 10^{13} \text{m}^{-3}$ for $N_{ref}$ in the remainder of this study. This is justified because the spread on number densities is large, as Housmans already noticed (cf. pg 51 in ref [201]). The circles in figure 8.2(a) are averages, but the spread in these kinds of measurements is illustrated well in figure 8.3(a).

Table 8.2: Backbone orientation and stretch time from XPP fit for slowest modes of iPP2 and iPP3 at $T = 138 ^\circ \text{C}$

<table>
<thead>
<tr>
<th>Material</th>
<th>$\lambda_0, \text{HMW} [\text{s}]$</th>
<th>$\lambda_0, \text{HMW} [\text{s}]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>iPP2</td>
<td>19.3</td>
<td>16.3</td>
</tr>
<tr>
<td>iPP3</td>
<td>750</td>
<td>92.5</td>
</tr>
</tbody>
</table>

Figure 8.2: Quiescent nucleus number density of iPP2 versus temperature (a) and flow-enhanced nucleus number density at $T = 138 ^\circ \text{C}$ for iPP2, as a function of shear time for different shear rates (b). Lines are to guide the eye.

8.2.3 Flow/iPP3

The second set of experiments is also taken from Housmans et al [16]. Figure 8.3(b) shows results from short-term shear experiments. The measured quiescent number density is a factor three larger than the prediction of Eq. 8.1 with $N_{ref}$ from Housmans et al. and therefore we have used an adjusted value of $N_{ref} = 4.05 \cdot 10^{12} \text{m}^{-3}$ in the remainder of this study.
8.3 Theory

8.3.1 Quiescent nucleation

We consider cylindrical precursors with length $2l$ and radius $r$, consisting of $n$ stems with length equal to that of the precursor and radius $r_0$ so that $r^2 = nr_0^2$. The precursors have a certain distribution in size. In this study we do not take into account a distribution of precursor and stem lengths; only one, uniform, length is considered. For a given $r_0$ and $l$, the precursors are now characterized by the single variable $n$. The size distribution $\rho(n)$ gives the number of precursors present per unit volume in the amorphous phase with a certain size $n$. Ziabicki and Alfonso derived a model for a similar system[54]. Their approach, based on a Fokker-Planck equation with the volume of the precursor as a stochastic variable, turns out to be unpractical for our purposes. A model with two variables, number of stems and precursor length, is even more complex. See appendix D.

The free energy change due to growth by crystallization of a precursor with size $n$ becomes

$$\Delta \tilde{F}(n) = -2n\pi r_0^2l \Delta h(1 - T/T_m) + 2n\pi r_0^2\sigma_e + 4\sqrt{n}\pi r_0 l \sigma_s$$  \hspace{1cm} (8.3)$$

where the first term accounts for the free energy decrease due to crystallization. The second and third terms are penalty terms due to surface tension on the ends and side of the precursor, respectively. $T_m$ is the thermodynamic melting point, $\Delta h$ is the heat of fusion per unit volume and $\sigma_e$ and $\sigma_s$ are the surface energies on the ends, with surface area $a_e$, and side of the precursor, with surface area $a_s$, respectively. Values for these constants for polypropylene were obtained from Monasse and Haudin[202] and are shown in table 8.3. $r_0$ is taken to be the characteristic size of a unit cell of the crystalline phase of polypropylene, $r_0 = 0.5$ nm. For other choices, results qualitatively similar to those presented in this study are obtained.

The free energy of nucleation as a function of the number of stems $n$ for a constant precursor length $l$ and temperature $T$ is shown in figure 8.5. It shows a maximum at $n = n^*$, below which the free energy has a positive slope and crystallization is unfavorable; precursors with size $n < n^*$ are
Figure 8.4: Schematic depiction of a cylindrical precursor and a stem being added to the precursor.

Table 8.3: Nucleation parameters for polypropylene

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta h$</td>
<td>$1.4 \cdot 10^5$ J/m$^3$</td>
</tr>
<tr>
<td>$\sigma_e$</td>
<td>$0.144$ J/m$^2$</td>
</tr>
<tr>
<td>$\sigma_s$</td>
<td>$9.2 \cdot 10^{-3}$ J/m$^2$</td>
</tr>
<tr>
<td>$T_m$</td>
<td>481 K</td>
</tr>
</tbody>
</table>

Figure 8.5: Free energy of nucleation of a precursor versus number of stems of the precursor, for constant precursor length $l = 10$ nm at $T = 138$ °C.

dormant. Above this critical size crystallization is favorable and precursors with $n > n^*$ are active. The critical size follows from

$$n = n^* : \quad \Delta \tilde{F}(n^*) = \max \Delta \tilde{F}(n)$$

(8.4)

Note that there is no barrier for nucleation in longitudinal direction because $\frac{\partial \Delta \tilde{F}}{\partial l}$ is not a function of $l$. Thus, if we talk about the critical size we always mean the critical number of stems. The total
number of active precursors can be obtained by integration of the size distribution over the precursors with number of stems greater than the critical number \( n^* \),

\[
N_{p,a}(T) = \int_{n^*(T,l)}^{\infty} \rho(n)dn
\]  

(8.5)

where we have introduced the size distribution function \( \rho(n) \equiv \frac{dN_p}{dn} \). From Eq. 8.4 it follows

\[
\frac{\partial \Delta \tilde{F}(n)}{\partial n} \bigg|_{n=n^*} = 0
\]  

(8.6)

And substituting Eq. 8.3 gives

\[
n^* = \left( \frac{1}{r_0} \frac{l \sigma_s}{\Delta h(1 - T/T_m)} \right)^2
\]  

(8.7)

Figure 8.6(a) shows the critical number of stems \( n^* \) versus precursor length for fixed temperature. Precursors with length \( l < l^* = \frac{\sigma_s}{\Delta h(1 - T/T_m)} \) form an interesting category. In the current model these precursors are allowed to become active, whereas one might argue that these precursors are unstable and can not become active because the free energy won by crystallization is not sufficient to overcome the surface tension, with an extra contribution due to dangling amorphous ends of the chains getting into a squeeze. Also, internal defects, which we have not considered, might have a relatively large negative contribution to \( \Delta h \) at small lengths. In short: the length to diameter ratio of these precursors is too small to overcome the surface tension at the ends of the precursor. The model might be too simplified below this critical length. The issue is avoided by fixing the precursor length in a quiescent melt at \( l_0 = 10 \) nm (such that \( l_0 > l^* \)) in the remainder of this study, then the critical size shows a monotonic decrease as the length of the precursors increases. The exact choice for \( l_0 \) is somewhat arbitrary. The results that we present in this study (validation with experiments and comparison to another model) hold for other choices for \( l_0 \), as long as \( l_0 > l^* \). For this choice of precursor length, the critical size versus temperature is shown in figure 8.6(b).

### 8.3.2 Precursor size distribution

We now derive the size distribution of precursors. With the critical precursor size as a function of temperature known from theory and the differential nucleus number density at a range of temperatures obtained from experiments, theory and experiment can be combined to obtain the number of precursors that become active at a certain value for the critical size. Assuming, in accordance with the idea of dormant precursors proposed by Janeschitz-Kriegl,[45, 196] that the size distribution is fixed, this gives us the precursor size distribution. Using the differential number density as a function of temperature, Eq. 8.2, and Eq. 8.7 for the critical size as a function of temperature, we obtain the following expression for size distribution at the critical size \( \rho(n^*) \)

\[
\int_{n^*(T)}^{\infty} \rho(n)dn = N_n(T)
\]

\[
\frac{d}{dn^*} \int_{n^*(T)}^{\infty} \rho(n)dn = -\rho(n^*) = \frac{\partial N_n}{\partial T} \frac{\partial T}{\partial n^*}
\]

\[
\rho(n^*) = c_N N_{ref} e^{-c_N \left(T_m(1-\sigma_s/(l\Delta h)-\sigma_s/(\sqrt{n^* r_0 \Delta h}))-T_{ref}\right)} \frac{\sigma_s T_m}{2\Delta h r_0 n^* \sqrt{n^*}}
\]  

(8.8)
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Figure 8.6: Critical number of stems as a function of precursor length at $T = 138$ °C (a) and critical number of stems as a function of temperature for a precursor length $l_0 = 10$ nm. (b)

In our model the size distribution of precursors does not change with temperature and thus the above equation is valid as a size distribution function,

$$
\rho(n) = c_N N_{ref} e^{-c_N(T_m(1 - \sigma_e/(\ell \Delta h) - \sigma_e/\sqrt{\pi \ell \Delta h}) - T_{ref})} \frac{\sigma_e T_m}{2 \Delta h r_0 n^2} \tag{8.9}
$$

The size distribution of precursors in the melt calculated using the above procedure for both iPP2 and iPP3 is shown in figure 8.7.

Figure 8.7: Size distribution of precursors for iPP2 and iPP3

8.3.3 Flow-enhanced nucleation

The effect of flow is modeled by increasing the length of the precursors by an amount of $\Delta l$. Precursors with length $l$ that are dormant in a quiescent melt (i.e. $n < n^\ast(l)$) may become active because, as
shown in figure 8.6(a), \( n^* \) for a precursor with length \( l + \Delta l \) is smaller than the critical size for a precursor with length \( l \); i.e. activation by flow occurs if \( n > n^*(l + \Delta l) \), where \( n^*(l + \Delta l) \) is the critical number of stems for a precursor with length \( l + \Delta l \).

The time evolution of the number of active precursors, i.e. the number of precursors pushed over the activation barrier per unit time, can be expressed in the following way

\[
\dot{N}_{p,a} = -\frac{dN_{p,a}}{dn^*} n^* - \frac{N_{p,a}}{\tau_{pn}}
\]

\[
= -\rho(n^*) \left( \frac{\partial n^*}{\partial l} \dot{l} + \frac{\partial n^*}{\partial T} \dot{T} \right) - \frac{N_{p,a}}{\tau_{pn}} \tag{8.10}
\]

where \( \dot{l} \) is the longitudinal precursor growth rate, the total length increase follows from integration over time of the growth rate, \( \Delta l = \int \dot{l} \, dt \). The first term accounts for the number of precursors activated by the flow per unit time. All simulations in this paper are in isothermal conditions and thus \( \dot{T} = 0 \), but the model can also be used to simulate non-isothermal cases. The second term comes from active precursors nucleating, which happens with a characteristic timescale \( \tau_{pn} \).

\[
\dot{N}_n = \frac{N_{p,a}}{\tau_{pn}} \tag{8.11}
\]

It is well known that microscopic pictures of iPP during flow-enhanced nucleation experiments show that all spherulites become visible at approximately the same moment in time, and that their diameters are nearly equal\[118, 203\]. This means that the large majority of nuclei is created at approximately the same moment in time. Furthermore, we have not observed significant numbers of spherulites during flow in our current and previous experimental work, even when the duration of flow was long enough to observe them with optical microscopy\[5, 118\]. This result agrees with X-ray measurements of Mahendrasingam et al. during film drawing of PET\[142, 204\]. They observed that, for high strain rates, crystallinity only started developing after the end of the draw. Based on these observations, we assume that the characteristic time of nucleation is much longer than the duration of flow in our short-term shear experiments and that nucleation is instantaneous in the absence of flow. Hence we set \( \tau_{pn} = \infty \) during flow and \( \tau_{pn} = 0 \) after flow. Balzano et al. did observe formation of fibrillar crystalline structures in iPP during flow, but the experimental conditions at which these were observed lie far out of the regime of flow-enhanced pointlike nucleation\[150\].

We notice that the precursor activation rate, Eq. 8.10, can be written as a factor times the longitudinal growth rate \( \dot{l} \) for isothermal flow-enhanced nucleation. This factor, \( -\rho(n^*) \frac{\partial n^*}{\partial T} \), is shown for a range of lengths in figure 8.8. Because this quantity does not vary largely (just a factor four) over the range of precursors lengths encountered in experiments (the maximum length reached is \( \sim 35 \) nm, see figure 8.12(b)), the creation rate of active precursors (in the absence of nucleation) is approximately proportional to the growth rate of the precursors.

\[
\dot{N}_{p,a} \sim \dot{l} \tag{8.12}
\]

It is well known that the high molecular weight (HMW) fraction of a polydisperse melt has a dominant influence on the flow-enhanced nucleation process\[15, 26, 205, 206\]. Steenbakkers and Peters found the fourth power of the average stretch of the primitive paths of chains in the HMW mode of the material (\( \Lambda \)) to be a good measure of the increase in nucleation rate\[5, 118\]. Graham and Olmsted found that a model based on the exponent of the average molecular stretch squared gives quantitative agreement with their Monte Carlo simulations\[62\]. Both approaches give very similar
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Figure 8.8: $-\rho(n^*) \frac{\partial n^*}{\partial t}$ versus $l$ for iPP2

results for the nucleation rate[61]. Following these studies, we take the growth rate of the precursors to be a function of the molecular stretch of the HMW tail of the material,

$$\dot{l} = c(\Lambda^4 - 1)$$  \hspace{1cm} (8.13)

which, because $\dot{N} \sim \dot{l}$, is similar to Steenbakkers’s nucleation rate (see also the section "Comparison to Steenbakkers’s model"). $c$ is a scaling parameter containing material properties, e.g. isotacticity and polydispersity. $\Lambda$ is calculated using the eXtended Pom-Pom (XPP) constitutive model. The performance of the Rolie-Poly model in our nucleation model is evaluated in appendix C. Equations for both constitutive models are given in appendix A. Similar results could be obtained by replacing $\Lambda^4$ with the recoverable strain, quantified by the second invariant of the deviatoric part of the elastic Finger tensor, $J_2(B^d_e)$, as in Zuidema et al. [46] because

$$J_2(B^d_e) = 9\Lambda^4 J_2(S^d)$$  \hspace{1cm} (8.14)

and $J_2(S^d)$, the second invariant of the deviatoric part of the orientation tensor, hardly changes as a function of shear time[5, 118]. In the "Alternative precursor growth model" section a different growth model, based on the work of Graham and Olmsted [61, 62] is evaluated.

8.4 Results

8.4.1 Model validation

In this section the present model is validated with results from short-term shear experiments presented in the "Experimental results" section. Final nuclei number densities from simulations and experiments are compared in figure 8.9. We observe a quantitative agreement between simulations and experiments. The scaling parameter $c$ differs by a factor of 10 between the materials, but the model gives good results with the same scaling parameter for different shear rates. The difference in $c$ might well be caused by the difference in isotacticity between the two materials; iPP2 has a higher isotacticity than iPP3 (97.5% versus 94.7%, see table 8.1) and might thus be more susceptible to flow-enhanced nucleation.
Figure 8.9: Number densities for (a) iPP2 and (b) iPP3 after experiments at 138 °C. Open symbols show measurements, filled symbols show simulations. Model parameters: $c = 2 \cdot 10^{-13} \text{ m/s}$ for iPP2, $c = 1.5 \cdot 10^{-14} \text{ m/s}$ for iPP3.

Figures 8.10 and 8.11 show the time evolution of the number of active precursors and nuclei of the simulations from figure 8.9. The number of nuclei shows an increase after flow because the stretch of the molecules takes some time to relax after the flow is ceased, which seems to contradict Steenbakkers's remark that all nuclei must have started growing at the same instant in time.[118] However, the maximum time span over which nuclei are created after flow is $\sim 50 \text{ s}$ (the measurement with shortest shear time in figure 8.11(a)). Multiplied by the lamellar growth rate of iPP at 138 °C, $1.5 \cdot 10^{-8} \text{ m/s}$,[16] this gives a maximum difference in radius of 0.75 $\mu\text{m}$ between the spherulites, which is below the resolution of optical microscopy. Therefore these simulations are not in disagreement with the experimental observation that all spherulites are of approximately the same size.
8.4.2 Saturation

A very interesting and surprising feature of the model is that the nucleus number density seems to reach a constant value for increasing shear time, a feature observed experimentally by for example Housmans et al. and Baert et al.[16, 24] The reason we observe saturation in simulations is explained below.

First, and most importantly, the molecular stretch (and with it the precursor growth rate \( \dot{\gamma} \)) as a function of shear time first increases rapidly, reaches a maximum and then relaxes towards a steady state, as shown in figure 8.12(a). Consequently, the precursor length \( l \) resulting from a shear experiment grows fast for increasing shear times when looking at short-term shear experiments, and as the shear times get larger, the length increase for the same increase in shear time gets smaller. This is depicted in figure 8.12(b). Precursor length versus time is shown for 5 experiments, with shear times of 4, 6, 8, 10 and 12 seconds. The difference in resulting precursor length between the experiments with \( t_s = 4 \) s and \( t_s = 6 \) s is \( \sim 3 \) nm, where the difference between the experiments with
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Figure 8.11: Number densities of active precursors (dashed lines) and nuclei (solid lines) versus time for iPP3 during experiments with different shear times at 138 °C. Model parameter: \( c = 1.5 \cdot 10^{-14} \) m/s. Two shear rates are shown: (a) \( \dot{\gamma} = 0.7 \) s\(^{-1}\), (b) \( \dot{\gamma} = 5 \) s\(^{-1}\).

\( t_s = 10 \) s and \( t_s = 12 \) s is only \( \sim 1 \) nm. In short: the average precursor growth rate over the full length of the experiment decreases with increasing shear time. Saturation is mostly caused by this effect. It is important to note that saturation already starts during the "softening" in \( \Lambda(t) \) before it reaches steady state. According to Housmans et al. the first normal stress difference and the shear viscosity reach their steady state much sooner than saturation.[16] Hence neither the rheology of the HMW tail nor that of the whole melt shows a correlation between steady-state behavior and saturation, as suggested by Martins et al. [207]

A second effect also has a contribution to the saturation effect, albeit smaller than the first one. The factor \( -\rho(n^*) \frac{\partial n^*}{\partial l} \) in Eq. 8.10 decreases after reaching a maximum at \( l = 30 \) nm (see figure 8.8, this precursor length corresponds to \( N_{p,a} = 2 \cdot 10^{13} \) m\(^{-3}\) as can be seen from figures 8.12(b) and (c)). Consequently, after that number of active precursors is reached the activation rate of precursors decreases.

Note that the number of nuclei versus shear time does not actually reach a plateau in our model. With increasing shear time, the activation rate of precursors becomes small, but not zero. At very long shear times the number of nuclei will reach a final value because the critical number of stems reaches 1, which means that every single stem will nucleate. From this point on \( n^* \) does not decrease anymore and thus the number of nuclei becomes constant. However, the length at which this happens lies far out of the range accessed in the simulations presented in this study. In experiments, regime 3 with oriented structures (see introduction) would be entered long before this happens.
Figure 8.12: (a) Molecular stretch, (b) precursor length and (c) number density of active precursors (dashed line) and nuclei (solid lines) versus time for short-term shear experiments with different shear times (4, 6, 8, 10 and 12 s) on iPP2, $\dot{\gamma} = 15 \text{ s}^{-1}$ at 138 °C

8.4.3 Comparison with Steenbakkers’s model

We compare simulation results from our model with the model presented by Steenbakkers and Peters[5, 118]. The flow-induced creation rate of nucleation precursors in this model can be simplified to

$$\dot{N}_{pf} = g_p (A^4 - 1) - \frac{N_{pf}}{\tau_p}$$  \hspace{1cm} (8.15)

where on the right hand side the first term represents the creation of precursors and the second term originates from precursors nucleating. $g_p$ is a scaling parameter, $N_{pf}$ is the number of flow-induced precursors. No dormant precursors exist in Steenbakkers’s model, all precursors formed by the flow are active according to the current definitions. Note that the flow-induced nucleation rate from Steenbakkers’s model thus has approximately the same structure as in our model, as follows from Eq. 8.12 with the growth rate as in Eq. 8.13. A part of Steenbakkers’s model that is not present in
the current model is that precursors form physical crosslinks, causing the relaxation time of the high molecular weight modes in the material to increase.[5, 46, 118] This increase is controlled by the parameter $a$,

$$\frac{\lambda_b}{\lambda_{0b}} = 1 + a(N_{pf} + N_{nf})$$

$$\frac{\lambda_s}{\lambda_{0s}} = 1 + a(N_{pf} + N_{nf})$$

where $\lambda_b$ and $\lambda_s$ are the backbone orientation and stretch times of the HMW tail as a result of the precursors forming crosslinks, respectively, and $\lambda_{0b}$ and $\lambda_{0s}$ are the orientation and stretch relaxation times of the HMW tail in a quiescent melt. $N_{nf}$ is the number of nuclei created by the flow, i.e. the number of flow-induced precursors that have turned into nuclei. We should also note that Steenbakkers and Peters needed the following empirical term to have their model predict saturation

$$g_p = g_{0p} \left(1 - \frac{N_{pf} + N_{nf}}{N_{f,\text{max}}}\right)$$

where $N_{f,\text{max}}$ is the maximum number of flow-induced precursors and nuclei, obtained from the saturation level in experiments. In the simulations that we did with this model, we do not require this term to obtain nucleus number densities that are in accordance with experiments (see figure 8.14(b)). This is caused by the fact that we have used the XPP constitutive model whereas Steenbakkers and Peters used the Rolie-Poly model to calculate the behavior of the polymer on continuum scale. Appendix C shows we experienced that the Rolie-Poly model does not perform as well as the XPP model in our nucleation model.

The creation rates of active precursors (in absence of nucleation) from both models are compared in figure 8.13. The dashed line show predictions of Steenbakkers’s model with no relaxation time increase, which means $\dot{N}_{p,a} = g_p(\Lambda^4 - 1)$. The dash-dotted line shows simulation results from Steenbakkers’s model with nonzero $a$ parameter, the solid line shows the model presented in this study. For all three cases the total final number densities are shown in figure 8.14. We observe that a model where the creation rate of active precursors is simply proportional to $(\Lambda^4 - 1)$ qualitatively agrees with experiments but underpredicts the final spherulite number density at the two higher shear rates. Both Steenbakkers’s model and the present model increase the prediction for the higher shear rates, the first by relaxation time increase because of the formation of physical crosslinks and the latter because the factor $-\rho(n^*) \frac{\partial n}{\partial t}$ increases for increasing length (up to $l = 30$ nm, see figure 8.8).
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8.4.4 Alternative precursor growth model

In this section we evaluate another growth model, i.e. another expression for the longitudinal precursor growth rate \( \dot{l} \). Graham and Olmsted performed Monte Carlo simulations of flow-induced nucleation and observed that the nucleation rate was well described by the relation [61]

\[
\dot{N} = \dot{N}_0 e^{(\eta(\Lambda^2 - 1))}
\]  

(8.18)

where \( \dot{N}_0 \) is the nucleation rate in absence of flow and \( \eta \) is a fitting parameter. In “Theory” we showed that the nucleation rate is approximately proportional to the precursor growth rate. We can thus use the relation found by Graham and Olmsted as a growth model,

\[
\dot{l} = c e^{(\eta(\Lambda^2 - 1))}
\]

(8.19)

where \( c \) and \( \eta \) are fitting parameters. The physical picture behind this growth model is that \( (\Lambda^2 - 1) \) represents the elastic energy stored in a chain. Simulation results for this growth model can be seen in figure 8.15. We observe a good agreement with simulations and experiments. However, we prefer the power law of molecular stretch, Eq. 8.13, because it requires just one scaling parameter to give equally good results.
Figure 8.14: Number densities for iPP2 after experiments at 138 °C. Open symbols show measurements, filled symbols show simulations with (a) and (b) Steenbakkers’s model and (c) our model. Constitutive behavior simulated with the XPP model. Model parameters: (a) \( g_p = 10^8 \text{ m}^{-3}\text{s}^{-1}, a = 0 \text{ m}^3 \), (b) \( g_p = 10^8 \text{ m}^{-3}\text{s}^{-1}, a = 10^{-13} \text{ m}^3 \), (c) \( c = 2 \cdot 10^{-13} \text{ m/s} \).
A model was derived for flow-enhanced nucleation based on the concept of a melt containing a fixed number of fibrillar flow-activatable nucleation precursors. Longitudinal precursor growth, causing activation of dormant precursors, is a function of molecular deformation: the average stretch of the primitive path of chains in the high molecular weight tail of the material, calculated from a rheological constitutive model. Both the Rolie-Poly and the eXtended Pom-Pom model were evaluated. The nucleation model was found to perform best in combination with the XPP model. Simulations of the model give quantitative agreement with experiments on two grades of iPP. Per material, a single scaling parameter suffices for the whole range of shear rates applied. The difference in scaling parameter between the two grades can be explained by the different isotacticities of the materials. Surprisingly, the model predicts saturation of the number density of nuclei with increasing shear time without any phenomenological terms. The model can also be applied to non-isothermal cases.

Acknowledgements

We would like to thank Prof. Dr. Han Slot for helpful discussions on the statistical size distribution. Also, we are thankful to Dr. Markus Gahleitner for kindly providing isotacticity, nucleus number density data and nucleus growth rate data for iPP2. This work was supported by the Dutch Technology Foundation (STW), grant no. 08083.
8.A  The XPP and Rolie-Poly models

This appendix is a slightly adapted form of section 3.3 from Steenbakkers. [118]

The Cauchy stress tensor for a polymer melt is written in the form

$$\sigma = -pI + \sum_{i=1}^{M} G_i (B_{c,i} - I)$$  \hspace{2cm} (8.20)$$

where $i = M$ indicates the mode with the longest relaxation time. The elastic Finger tensor $B_{c,i}$ of mode $i$ follows from

$$\nabla B_{c,i} = -A_i \cdot B_{c,i} - B_{c,i} \cdot A^T$$  \hspace{2cm} (8.21)$$

The triangle denotes the upper convected derivative and $A_i$ is the slip tensor of mode $i$, which describes the non-affine deformation of the corresponding molecules. Several constitutive models can be written in this form with different expressions for $A_i$. [208] The constitutive models utilized in this paper are listed in table 8.4. The Giesekus model is shown for comparison.

Table 8.4: Slip tensors for the Giesekus [209, 210], XPP [130], Rolie-Poly [129] and finitely-extensible (FE) Rolie-Poly [211] models.

<table>
<thead>
<tr>
<th>Model</th>
<th>$A_{1,i}$</th>
<th>$A_{2,i}$</th>
<th>$A_{3,i}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Giesekus</td>
<td>$\frac{\alpha_i}{2\lambda_{b,i}}$</td>
<td>$-\frac{(1-\alpha_i)}{2\lambda_{b,i}}$</td>
<td>$\frac{1-2\alpha_i}{2\lambda_{b,i}}$</td>
</tr>
<tr>
<td>XPP</td>
<td>$\frac{\alpha_i}{2\lambda_{b,i}}$</td>
<td>$-\frac{1-\alpha_i}{2\lambda_{b,i}}$</td>
<td>$\frac{1-\alpha_i-3\alpha_i \Lambda_i^2 S_i \cdot S_i}{2\lambda_{b,i} \Lambda_i^4} + \frac{1}{\lambda_{b,i}} \left(1 - \frac{1}{\Lambda_i^4}\right)$</td>
</tr>
<tr>
<td>Rolie-Poly</td>
<td>0</td>
<td>$-\frac{1}{2\lambda_{b,i}} - \frac{\beta_i \Lambda_i^{4\lambda}}{\lambda_{b,i}^2} \left(1 - \frac{1}{\Lambda_i^4}\right)$</td>
<td>$\frac{1}{2\lambda_{b,i}} + \frac{1+\beta_i \Lambda_i^{4\lambda}}{\lambda_{b,i}^2} \left(1 - \frac{1}{\Lambda_i^4}\right)$</td>
</tr>
<tr>
<td>FE Rolie-Poly</td>
<td>0</td>
<td>$-\frac{1}{2\lambda_{b,i}} - k_s \frac{\beta_i \Lambda_i^{4\lambda}}{\lambda_{b,i}^2} \left(1 - \frac{1}{\Lambda_i^4}\right)$</td>
<td>$\frac{1}{2\lambda_{b,i}} + k_s \frac{1+\beta_i \Lambda_i^{4\lambda}}{\lambda_{b,i}^2} \left(1 - \frac{1}{\Lambda_i^4}\right)$</td>
</tr>
</tbody>
</table>

The elastic Finger tensor is taken equivalent to the conformation tensor, following Leonov. [212--214] The orientation tensor

$$S_i = \langle \vec{n}_i \vec{n}_i \rangle = \frac{B_{c,i}}{\text{tr}(B_{c,i})}$$  \hspace{2cm} (8.22)$$

gives the average molecular orientation; $\vec{n}_i$ is a unit vector, tangent to the primitive path of a chain, and the angle brackets indicate an average over the orientation distribution. If the stretch of the primitive path is assumed homogeneous, it is described by the scalar stretch parameter

$$\Lambda_i = \sqrt{\frac{\text{tr}(B_{c,i})}{3}}$$  \hspace{2cm} (8.23)$$

which follows from $B_{c,i} = 3\Lambda_i^2 S_i$. [215]

In the XPP model, the backbone stretch relaxation time is dependent on the molecular stretch,

$$\lambda_s,i = \lambda_{0,s,i} e^{-\nu_i (\Lambda - 1)}$$  \hspace{2cm} (8.24)$$

where $\nu_i = \frac{2}{q_i}$. 

The parameter $k_s$ was introduced into the Rolie-Poly model by Kabanemi and Hétu to make the chains finitely extensible.[211] $k_s$ is a nonlinear spring coefficient, given by

$$k_s(\Lambda) = \frac{(1 - 1/\Lambda_{\text{max}}^2)(3 - \Lambda^2/\Lambda_{\text{max}}^2)}{(1 - \Lambda^2/\Lambda_{\text{max}}^2)(3 - 1/\Lambda_{\text{max}}^2)}$$

where $\Lambda_{\text{max}}$ is the maximum backbone stretch possible.

### 8.8 Parameters for the constitutive models

For both materials, the XPP and Rolie Poly model were fitted to extensional viscosity data, see figures 8.16 and 8.17. The resulting relaxation times are shown in tables 8.5 and 8.6.

For the Rolie Poly model, we used $\beta = 0$, representing no convective constraint release, as this gives the best results.[5, 118] Consequently the parameter $\delta$ plays no role. For the modified XPP model, we used $\alpha_i = 0.1/q_i$.

![Figure 8.16: Extensional viscosity for iPP2 at 180 °C, symbols show measurements, dashed lines show the linear viscoelastic response, solid lines show (a) XPP, (b) Rolie-Poly and (c) Rolie-Poly with finite extensibility](image-url)
A model for flow-enhanced nucleation based on fibrillar dormant precursors

Figure 8.17: Extensional viscosity for iPP3 at 220 °C, symbols show measurements, dashed lines show the linear viscoelastic response, solid lines show (a) XPP, (b) Rolie-Poly and (c) Rolie-Poly with finite extensibility.

Table 8.5: Parameters for XPP and Rolie Poly models for iPP2 at 138 °C

<table>
<thead>
<tr>
<th>$\lambda_{0,i}$ [s]</th>
<th>$\lambda_{0,i}$ [s] (XPP)</th>
<th>$q_i$ (XPP)</th>
<th>$\lambda_{0,i}$ [s] (Rolie-Poly)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>0.01</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0.06</td>
<td>0.06</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0.36</td>
<td>0.36</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2.16</td>
<td>2.16</td>
<td>0</td>
<td>0.14</td>
</tr>
<tr>
<td>12.9</td>
<td>1.75</td>
<td>7.92</td>
<td>1.1</td>
</tr>
<tr>
<td>77.8</td>
<td>16.3</td>
<td>11.9</td>
<td>7.1</td>
</tr>
</tbody>
</table>

8.8.1 iPP2
Best fits are obtained for an XPP model with four non-stretching modes and two stretching modes, and a Rolie-Poly model with three non-stretching and three stretching modes. Reptation times are
A model for flow-enhanced nucleation based on fibrillar dormant precursors

Table 8.6: Parameters for XPP and Rolie Poly models for iPP3 at 138 °C

<table>
<thead>
<tr>
<th>$\lambda_{b,i} \ [s]$</th>
<th>$\lambda_{0b,i} \ [s] \ (XPP)$</th>
<th>$q_i \ (XPP)$</th>
<th>$\lambda_{w,i} \ [s] \ (Rolie-Poly)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0052</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0345</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.174</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.840</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.01</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>19.3</td>
<td>23.1</td>
<td>2.4</td>
<td>3.86</td>
</tr>
<tr>
<td>104</td>
<td>61.6</td>
<td>6.2</td>
<td>38.6</td>
</tr>
<tr>
<td>750</td>
<td>92.5</td>
<td>14.9</td>
<td>231</td>
</tr>
</tbody>
</table>

from Housmans et al.[201] backbone stretch times for the Rolie-Poly model are equal to the ones used by Steenbakkers and Peters.[5, 118]

8.B.2 iPP3

Best fits are obtained for an XPP model and a Rolie-Poly model both with five non-stretching and three stretching modes. Reptation times are taken from Swartjes.[200] The maximum stretch parameter in the finitely extensible Rolie-Poly model $\Lambda_{\text{max}} = 5$. 

Constitutive behavior from Rolie-Poly model

One would expect the Rolie-Poly model (developed for linear polymers) to be more suitable than the XPP model (developed for branched polymers) to describe iPP, since iPP is a linear polymer. In this section we evaluate our nucleation model with the constitutive behavior simulated with the Rolie-Poly model (equations shown in appendix A). Simulation results are presented in figure 8.18. We observe that the simulations and experimental results are not in as close agreement as when using the XPP model. The predictions can be slightly improved by turning on convective constraint release (i.e. setting $\beta \neq 0$), but this leads to extensional viscosity predictions that are not physical (i.e. lower than the linear viscoelastic response for some strain rates). A possible cause for the poor performance is the high molecular stretch the Rolie-Poly model yields, compare figure 8.19 and figure 8.12(a). A possible solution to this problem might be using a finitely extensible Rolie-Poly model (equations can be found in appendix A). Simulation results are shown in figure 8.20. From this figure we conclude that neither the infinitely extensible, nor the finitely extensible Rolie-Poly model performs nearly as well as the XPP model. For this reason, we have used the XPP model throughout this study.

![Figure 8.18: Number densities for (a) iPP2 and (b) iPP3 after experiments at 138 °C. Open symbols show measurements, filled symbols show simulations. Rheological behavior simulated with the Rolie-Poly model. Model parameters: $c = 1 \cdot 10^{-14}$ m/s for iPP2, $c = 5 \cdot 10^{-17}$ m/s for iPP3.](image)
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Figure 8.19: Molecular stretch versus time for shear experiments on iPP2, $\dot{\gamma} = 15 \text{ s}^{-1}$ at 138 °C. Rheological behavior simulated with the Rolie-Poly model. Behavior for different shear times (4, 6, 8, 10 and 12s) is shown.

Figure 8.20: Number densities for (a) iPP2 and (b) iPP3 after experiments at 138 °C. Open symbols show measurements, filled symbols show simulations. Rheological behavior simulated with the finitely extensible Rolie-Poly model. Model parameters: $c = 2 \times 10^{-12} \text{ m/s}$ for iPP2, $c = 5 \times 10^{-13} \text{ m/s}$ for iPP3.

8.D Precursors with a distribution of lengths

In this appendix the expansion of our theory to two dimensions is investigated. This expansion means that, instead of taking just one value for the precursor length $l$ and varying the number of stems, the precursors have a distribution both in length and in number of stems. To this purpose, a new dimensionless variable $s$ is introduced and the length of a stem/precursor is expressed as $l = s l_0$ with $l_0$ a yet to be determined reference length. We simplify by assuming that stems only interact with precursors of the same length. The only growth mechanism for precursors in a quiescent melt is stem addition, in contrast to the work by Graham and Olmsted who considered a similar system.
Because the size distribution $\rho$ now is a function of both $n$ and $s$, the procedure we used in the "Theory" section where $\rho$ was obtained by combining theory and experiment is no longer applicable. Therefore, we investigate a different method to obtain a precursor size distribution. A method to obtain a size distribution from a Fokker-Planck equation for clusters (equivalent to precursors in our case) that are described by one characteristic measure, the number of kinetic units in a cluster (equivalent to the number of stems) was presented by Ziabicki and Alfonso.[54] As a result of our assumption that stems only interact with precursors of the same length, each species $i$ of stems and precursors with length $l_i = s_i l_0$ has a size distribution density $\rho(n, s_i)$, determined by a Fokker-Planck equation that is decoupled from the size distributions of other species. If stems and precursors of different lengths were allowed to interact, the size distributions of all species would be determined by a system of coupled Fokker-Planck equations with a large number of unknown diffusion parameters, making the model useless for current purposes.

The Fokker-Planck equation for species $i$ is

$$\frac{\partial \rho(n, s_i, t)}{\partial t} - \frac{\partial}{\partial n} \left[ D_{Gr}(n, s_i) \left( \frac{\partial \rho(n, s_i, t)}{\partial n} + \rho(n, s_i, t) \frac{\partial \Delta \tilde{F}(n, s_i)}{\partial n} \right) \right] = 0 \quad (8.26)$$

where $D_{Gr}$ is the coefficient of growth diffusion and $\Delta \tilde{F}$ is the driving force of crystallization of a precursor with sizes $n, s_i$. A steady state distribution density can be derived following the same procedure as Ziabicki and Alfonso [54];

$$\frac{\partial \rho_{st}(n, s_i, t)}{\partial t} = \frac{\partial}{\partial n} \left[ D_{Gr}(n, s_i) \left( \frac{\partial \rho_{st}(n, s_i, t)}{\partial n} + \rho_{st}(n, s_i, t) \frac{\partial \Delta \tilde{F}(n, s_i)}{\partial n} \right) \right] = 0 \quad (8.27)$$

$$\frac{\partial \rho_{st}(n, s_i)}{\partial n} + \frac{\rho_{st}(n, s_i)}{kT} \frac{\partial \Delta \tilde{F}(n, s_i)}{\partial n} = \frac{C}{D_{Gr}(n, s_i)} \quad (8.28)$$

where $C$ is a constant. We define $A(n, s_i) = \frac{1}{kT} \frac{\partial \tilde{F}(n, s_i)}{\partial n}$. As an ansatz for the steady state distribution density we take

$$\rho_{st} = \Phi(n, s_i) \exp \left( \int_n^{n_{\text{max}}} A(n', s_i) dn' \right) \quad (8.29)$$

where $n_{\text{max}} \gg n^*$ is a maximum for the precursor size considered. Substituting into Eq. 8.28 gives

$$\frac{\partial \Phi(n, s_i)}{\partial n} = \frac{C}{D_{Gr}(n, s_i)} \exp \left( - \int_n^{n_{\text{max}}} A(n', s_i) dn' \right) \Phi(n, s_i) = \Phi(n_{\text{max}}, s_i) - C \int_n^{n_{\text{max}}} \frac{1}{D_{Gr}(n', s_i)} \exp \left( - \int_n^{n_{\text{max}}} A(n'', s_i) dn'' \right) dn' \quad (8.30)$$

After applying the boundary conditions,[54]

$$\rho_{st}(n = 1, s_i) = \rho_1(s_i) \quad (8.31)$$
$$\rho_{st}(n = n_{\text{max}} \gg n^*, s_i) = \Phi(n_{\text{max}}, x_i) = 0 \quad (8.32)$$
the steady state distribution for species \( i \) becomes

\[
\rho_{st}(n, s_i) = \frac{\rho_1(s_i) \exp\left(\frac{\Delta F(1, s_i)}{kT}\right) \int_{n}^{n_{max}} \exp\left(\frac{\Delta F(n, s_i)}{kT}\right) / D_{gr}(n', s_i)dn'}{\exp\left(\frac{\Delta F(n, s_i)}{kT}\right) \int_{1}^{n_{max}} \exp\left(\frac{\Delta F(n', s_i)}{kT}\right) / D_{gr}(n', s_i)dn'}
\]

(8.33)

where we have introduced \( \rho_1(s) \), the steady state distribution of single stems as a function of stem length. \( \rho_1 \) can be expressed as \( \rho_1 = \phi(s)\rho_0 \), where the weighting function \( \phi(s) \) gives the fraction of stems that have length \( s \) (\( \int_{0}^{\infty} \phi(s)ds = 1 \)) and \( \rho_0 \) is the total amount of single stems. The free energy of nucleation \( \Delta \tilde{F} \) is given by Eq. 8.3 and schematically depicted in figure 8.5. The coefficient of growth diffusion \( D_{gr} \) can be presented in the form [54]

\[
D_{gr} = D_0 \left(\frac{T}{T_m}\right) \sqrt{\frac{n}{\tau_{gr}}}
\]

(8.34)

where \( D_0 \) is a constant and \( \tau_{gr} \) is the relaxation time related with self-diffusion of kinetic units subject to aggregation. The factor \( \sqrt{n} \) accounts for the number of sites available for attachment/detachment of a stem on the surface of an \( n \)-sized precursor. All terms of \( D_{gr} \) will divide out in the expression for the steady state size distribution, except for \( \sqrt{n} \). The total number of active precursors can now be calculated by integration of the steady state size distribution over all precursor lengths and the range of \( n \) for which precursors are active, i.e. \( n > n^* \) up to a certain maximum value \( n_{max} \).

\[
N_{p,a} = \int_{1}^{\infty} \int_{n^*(s)}^{n_{max}} \rho(n, s)dn ds
\]

(8.35)

Figure 8.21 shows the steady state size distribution \( \rho_{st} \) for one species; \( \phi = 1 \) thus \( \rho_0 = \rho_1 \). \( n_{max} \) is chosen such that increasing \( n_{max} \) does not visibly change the solution. The deterministic size distribution, calculated using the method explained in the "Theory" section, is shown for comparison. \( \rho_0 = \rho_1 \) was chosen such that both the statistical and deterministic size distributions have an equal amount of precursors with size \( n = 1 \).
A model for flow-enhanced nucleation based on fibrillar dormant precursors

Figure 8.21: Solid line: steady state stochastical size distribution, for one species of precursors with \( s_{0} = 10^{-8} \) m. \( n_{\text{max}} = 100 \) and \( \rho_{0} = \rho_{1} = 2 \cdot 10^{14} \). Dashed line shows the precursor size distribution for iPP2 at 138 °C as determined by the method from the ”Theory” section for comparison.

Unfortunately, at this moment this steady state distribution is of no use for the flow-enhanced nucleation model presented in this study, for the following reasons. First, the statistical model actually describes sporadic nucleation, whereas the nucleation is mainly athermal in flow-induced crystallization. Second, the main motivation for deriving the statistical size distribution was to be able to extend the present model to two dimensions. Because we have no way to directly determine the weighting function \( \phi(s) \), we cannot derive a unique function for the two-dimensional precursor size distribution and therefore the statistical approach, as the deterministic approach, is only applicable to the one-dimensional case.
Chapter 9

Conclusions and Recommendations

9.1 Conclusions

This research was aimed at modeling various aspects of the flow-induced crystallization process, compare with experimental results in order to validate the modeling, and get quantitative predictions on the scale of different crystalline structures. In this chapter main conclusions are summarized and recommendations are given for future work.

*Flow-enhanced point-like nucleation and rheology*

- In terms of linear rheological properties, a suspension of soft spheres is an accurate representation of growing spherulites in a polymer melt. The rheological properties of such a system at any crystalline volume fraction can be accurately calculated if the properties of the polymer melt and the crystallized material are known.
- The viscosity upturn time in continuous shear flow experiments can be predicted by combining the above described suspension model with a phenomenological nucleation model.
- In continuous extension flow at high extension rates, one also obtains very accurate predictions for the upturn time, however this is for the wrong reason. The model, lacking finite extensibility, overpredicts the viscosity upturn due to strain hardening in the longest chains in the material. This event coincides exactly with the appearance of shish, which cause the viscosity upturn in experiments. Because the observed viscosity upturn happens in such a short time that crystals do not have time to fill any space, this is a first indication that shish affect rheology much stronger than smooth fibers.
- Apparent saturation of nucleation density with shear time in short-term shear experiments is a rheological effect. Because of the stress overshoot after flow start-up, nucleation rate is strongly enhanced at short times. In steady state conditions, nucleation rate reaches a plateau. Because this plateau value is much lower than the value during the stress overshoot, nucleation density (i.e. the integral of nucleation rate over flow time) appears to saturate with flow time.
- Rheological measurements in plate-plate geometry are strongly dominated by material near the edge of the sample. Therefore, disturbances in the flow field at the edges which result in enhanced crystallization rates can affect measurements in such a way that the measured rheology is not an accurate representation of the bulk material.
Conclusions and Recommendations

A model that departs from a reservoir of precursors which can be activated by the effect of temperature or flow describes flow-enhanced nucleation experiments, by having the growth speed of precursors scale with stretch on the continuum scale.

**Formation and crystallization kinetics of shish-kebab structures**

- The crystallization kinetics of oriented crystalline structures are strongly influenced by temperature increase due to latent heat release and conformational changes, both affecting crystal growth rate. By taking these effects into account, crystallization kinetics can be described quite accurately.

- The model described above can be applied in a reversed manner; by fitting the model to experiments, we can extract the line nucleation density for kebabs (i.e., specific shish length). Doing this reveals that for slit flow experiments, shish density seems to saturate around $10^{12} - 10^{13}$ m/m$^3$, in accordance with values found in literature [112] whereas for experiments in extensional flow, the shish density can reach as high as $10^{14}$ m/m$^3$.

- The crystallization kinetics and final parent/daughter ratio of shish-kebabs can be described with a model in which daughter lamellae nucleate on the parents, and incorporating the effect of parents having increased growth rate due to conformation changes shortly after flow.

- Irrespective of flow rate or time, the specific shish length within the shear layer, formed in a channel flow, is always the same. This is caused by a self-regulating effect. Shish increase the viscosity of the melt, thus lowering local deformation rate and arresting shish growth.

- The volume fraction of crystals at which shish start to significantly influence the rheology on a macroscopic scale is very low ($\approx 5\%$). This indicates the influence of shish can be felt on quite a long distance from the shish themselves, possibly caused by "hairs", i.e., chains protruding from the shish into the melt.

- A model for longitudinal shish growth with growth velocity directly proportional to shear rate, and viscosity increase implemented in an empirical way, is able to describe experimental results in terms of morphology, rheology, and crystallization kinetics.
9.2 Recommendations

- Throughout this thesis use has been made of a phenomenological crystallization model, coupling flow-induced nucleation rate to stretch on a continuum level. Although this approach is quite capable of describing experimental data in a large range of flow conditions with a small number of parameters, it lacks predictive qualities. This was demonstrated by the need to adapt the nucleation model to predict any structure formation for flows with very high shear rates and short shear times (Chapter 7). Unfortunately a fundamental understanding of the flow-induced nucleation process is still lacking. The obvious way forward is molecular dynamics simulations, but these are notoriously hard to perform and generally also feature some adjustable parameters [61, 62]. In my opinion, a second promising route is basic flow-enhanced nucleation experiments (at low shear rates) on mono-disperse or bi-disperse materials. In this way at the very least our hypothesis can be tested that the relevant timescale is the backbone stretch of the longest chains in the material.

- The current implementation of the effect of a suspension of shish on rheology is very crude. A big step forward to quantitatively testing the shish growth model presented in Chapter 7 would be a calculation of the macroscopic properties of a suspension of "hairy" shish. One could think of using Finite Element Simulations of particles suspended in a viscoelastic medium to calculate the effect on macroscopic properties at varying shear rates.

- The simulations presented in Chapter 7 show a strong discrepancy with experiments at short times, i.e. during flow and shortly hereafter. Specifically, the crystallinity is experimentally observed to grow at a much faster rate than our model predicts. A possible cause is the relation between conformation and crystal growth rate, which is now implemented in an empirical way via an exponential decay in time based on calculations presented in Chapter 5. However, in these calculations it was assumed that a certain amount of crystalline structure was present at the end of flow. The simulations presented in Chapter 7 obviously do not reach this amount of structure at the end of flow. Perhaps the empirical exponential decay function needs to be refined. Experimentally determining this function is not possible with the current experimental techniques, but a refinement of the model might be sought in an additional increase of growth rate at small shish radius, because the "hairs" protruding from shish into the melt, having their mobility decreased, are more prone to crystallize.

- In the experimental conditions relevant for the modeling in this thesis, one crystal modification always dominated. In practice however, a solidifying melt often encounters conditions which may result in a final morphology that consists of a combination of multiple crystal modifications, for example the $\alpha$, $\gamma$, and meso-phases in iPP. To fully grasp production processes, it would be desirable to also model the formation of these different phases. Such a model has been developed for quiescent conditions [151], with expressions similar to the ones used in the multi-morphology model for iPP in this thesis. Incorporation of the multi-phase model with the model for shish formation presented in Chapter 7 would be a useful exercise to test the hypotheses in both of these models.
References


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<th>Reference</th>
<th>Title</th>
<th>Journal/Source</th>
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References


References


Samenvatting

Semi-kristallijne polymeren, waaronder polyethyleen (PE) en isotactisch polypropyleen (iPP), vormen een klasse van materialen met goede verwerkbaarheid en eigenschappen voor een relatief lage prijs. Uiteindelijke eigenschappen na verwerking in de smelt zijn een direct gevolg van de kristallijne microstructuur, die op zijn beurt sterk afhankelijk is van de condities die het materiaal ondervindt tijdens stromen en stollen. Om eigenschappen te kunnen sturen, is daarom de samenhang tussen verwerkingscondities en uiteindelijke kristallijne structuur van belang. Dit proefschrift is erop gericht het effect van stroming op de uiteindelijke kristallijne structuur te kwantificeren, alsmede de kinetiek van het kristallisatieproces tijdens en na stroming.

Stromingsgeïnduceerde kristallisatie kan opgedeeld worden in twee regimes.

Voor milde stromingscondities blijft het effect van de stroming beperkt tot een toename van het aantal kiemen waaruit nuclei groeien. Dit leidt tot een sneller kristallisatieproces, maar de uiteindelijke morfologie blijft isotroop. Voor zulke condities is reometrie uitermate geschikt om het effect van stroming op structuur te onderzoeken. In dit proefschrift wordt een methode gevalideerd om de viscositeitsopbouw van een dergelijk systeem te modelleren, door uit te gaan van een suspensie van bolvormige deeltjes in een visco-elastische matrix. Door dit model te combineren met een fenomenologisch model voor stromingsgeïnduceerde nucleatie kan een nauwkeurige voorspelling worden gedaan van de viscositeitsopbouw tijdens stroming met constante afschuifsnelheid. Deze aanpak laat tevens zien dat de verzadiging van nucleatiedichtheid met toenemende stromingstijd kan worden verklaard vanuit een puur reologisch oogpunt. Naast het gebruik van een fenomenologisch model dat stromingsgeïnduceerde nucleatie direct koppelt aan macroscopische deformatie, wordt een alternatief model gepresenteerd dat uitgaat van een vast reservoir gevuld met precursors van verschillende grootte. Om kiemen voor nucleatie te worden moeten deze precursors een barrière overwinnen die gerelateerd is aan hun grootte. Het aantal kiemen kan zodoende worden verhoogd door verlaging van temperatuur (waarmee de barrière omlaag gaat), of verhoging van de stroming (waardoor de precursors in lengte groeien).

Bij sterkere stromingscondities wordt niet alleen het aantal kiemen verhoogd, maar worden ook georiënteerde kristalstructuren gevormd, zogeheten shish-kebabs. De kritische stromingscondities voor het ontstaan van zulke structuren is een belangrijk punt in stromingsgeïnduceerde kristallisatie. In dit proefschrift wordt aangetoond dat deze structuren in uniaxiale rekstroming verschijnen op het moment dat rekversteviging optreedt in de hoog moleculaire staart van het polymer. Door middel van experimenten met de RheoDSC, een opstelling waarin reometrie en Differential Scanning Calorimetry gecombineerd worden uitgevoerd, wordt aangetoond hoe het verschijnen van zulke structuren kan worden herkend in een reologische meting.
Reometrie is bij uitstek geschikt om stromingsgeïnduceerde kristallisatie te onderzoeken in homogene stromingsvelden onder milde stromingscondities. Echter, voor condities die meer relevant zijn voor praktische verwerkingsprocessen is een andere aanpak vereist. In dit proefschrift is gekozen voor een opstelling waarin de smelt, opgesloten in een kanaal tussen twee simultaan beweegbare zuigers, een Poiseuille stroming kan worden opgelegd. Door de hoge afschuifsnelheden wordt aan de wanden van het kanaal een laag met shish-kebabs gevormd. De dikte van deze laag neemt toe met sterkere, of langere, stroming. Door middel van zeer snelle (30 beelden per seconde) in-situ röntgendiffractie metingen kan de kristalliniteit bepaald, ook onder condities waarin een belangrijk deel van de structuur binnen enkele seconden groeit. Optische microscopie en transmissie elektronenmicroscopie zijn gebruikt om respectievelijk de laagdikte en structuur van shish-kebabs in kaart te brengen.

Met behulp van deze opstelling is de kristallisatiekinetiek van shish-kebab structuren in iPP onderzocht. Naast shish en kebabs vindt men in iPP ook een derde morfologie, genaamd dochters, die loodrecht groeien op de kebabs. Om de kristallisatie van de verschillende morfologieën te beschrijven zijn de veelgebruikte Schneider vergelijkingen aangepast. Volume wordt verdeeld tussen kebabs en dochters gebaseerd op hun momentane groeisnelheid, die sterk afhangt van ketenconformatie en temperatuur. De enige parameter in dit model die verandert per experiment is de specifieke shish lengte. Door deze parameter te bepalen kan de precieze structuur als functie van de stromingscondities gekwantificeerd worden.

Analyse van de gemiddelde kristallisatiekinetiek in de georiënteerde laag toont aan dat deze (voor de onderzochte stromingscondities) verrassend genoeg niet afhangt van stromingsnelheid of tijd. Dit resultaat toont het bestaan aan van een interessant zelfregulerend effect: doordat de viscositeit toeneemt naarmate meer structuur gevormd wordt, vriest de structuur in en voorkomt zo verdere groei. Er is een model geformuleerd dat formatie, verzadiging en kristallisatie van shish beschrijft. Het model levert een nauwkeurige beschrijving van experimenten in termen van morfologie, kristallisatiekinetiek, en viscositeit.
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Even though 4.22 is definitely not the best place to get work done, I would not have traded my spot for one in any other office. I always loved coming to the university, for which I have to thank all my (former) office mates: Martin, Marc, Harm, Enrico, Emanuele, Dirk, Dario, Amin, Nick, Sam, and Leon. Additionally I owe thanks to Zhe and Martin for their experimental expertise, which was indispensable to half of this thesis. Lambert, bedankt voor de broodnodige potjes squash om het hoofd leeg te maken. Helaas zullen we ze moeten verplaatsen naar de avonduren; ik hoop dat ons niveau niet blijft dalen naarmate de dag vordert.

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Peter
April 2014

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Curriculum Vitae

Peter Cornelis Roozemond was born on 20 March 1986 in Hazerswoude, The Netherlands. He finished his pre-university secondary school in 2004 at the Sint Oelbert Gymnasium in Oosterhout, where he graduated (cum laude) in subject clusters Science&Technology and Science&Health. He then enrolled in the Mechanical Engineering Department at the Eindhoven University of Technology, where he received his Bachelor's Degree in 2007. His Bachelor Final Project was performed in the Polymer Technology group on a 1D model for the electrospinning of viscoelastic fluids, which he enjoyed so much that he decided to enroll for his Master's degree in the same group. During his Master’s he joined the group of Prof. Norman J. Wagner at the University of Delaware, USA, for an internship of four months on the modeling of shear-banding fluids in cone-plate geometry. He also completed the Technical Management Certificate at the University of Eindhoven. He received his Master's degree (cum laude) in 2010 on the thesis entitled "A model for flow-enhanced nucleation based on fibrillar dormant precursors", in the group of Prof. Han Meijer under the supervision of Prof. Gerrit Peters.

After completion of his Master's degree, Peter took a position as a PhD student under supervision of Prof. Gerrit Peters in the Structure and Rheology of Complex Fluids group at the Eindhoven University of Technology, which has resulted in the present thesis. During his PhD he successfully completed the postgraduate course Register Polymer Science of the National Dutch Research School PTN (Polymeer Technologie Nederland) and was awarded the title of Registered Polymer Scientist in October 2013.
List of Publications

This thesis has resulted in the following publications:


- P.C. Roozemond, M. van Drongelen, L. Verbelen, P. Van Puyvelde, and G.W.M. Peters. "Flow-induced crystallization studied in the RheoDSC device: quantifying the importance of edge effects," *In preparation*


Additionally, the author has contributed to a number of publications outside of this thesis:
