Modeling flow-induced crystallization in isotactic polypropylene at high shear rates

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Synopsis

A model is presented to describe flow-induced crystallization in isotactic polypropylene at high shear rates. This model incorporates nonlinear viscoelasticity, compressibility, and nonisothermal process conditions due to shear heating and heat release due to crystallization. Flow-induced nucleation occurs with a rate coupled to the chain backbone stretch associated with the longest mode relaxation time of the polymer melt, obtained from a 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 formation of oriented fibrillar crystals (known as “shish”) is implemented in a phenomenological manner; shish act as a suspension of fibers with radius equivalent to the radius of the shish plus the attached entangled molecules? The model is implemented in a 2D finite element code and validated with experimental data obtained in a channel flow geometry. Quantitative agreement is observed in terms of pressure drop, apparent crystallinity, parent/daughter ratio, Hermans’ orientation, 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. © 2015 The Society of Rheology.

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I. INTRODUCTION

Flow-induced crystallization (FIC) during processing of semicrystalline polymers determines to a great extent the final product properties [cf. Bernland et al. (2010); Fujiyama and Wakino (1988); Schrauwen et al. (2004b)]. 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 [Pennings (1977); Pennings and Kiel (1965)], and later also in polymer melts [Keller and Mackley (1974)].

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The formation of these structures has a big influence on the morphology of injection-molded products [Fujiyama and Wakino (1988); Schrauwen et al. (2004b)]. 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 (typically created by shear rates in excess of $\sim 100 \text{s}^{-1}$), followed by a fine-grained layer with a high nucleation density (shear rates of $\sim 10$–$100 \text{s}^{-1}$) and finally a core with large spherulites [Housmans et al. (2009b); van Meerveld et al. (2004)]. 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 [Fernandez-Ballester et al. (2012); Kumaraswamy et al. (1999); Liedauer et al. (1993); Ma et al. (2013); Seki et al. (2002)].

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 $\gamma^2 t_s$, with $\gamma$ the shear rate and $t_s$ flow time, to the density of shish [Eder and Janeschitz-Kriegl (1997); Liedauer et al. (1993)]. 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 [Roozemond and Peters (2013); Steenbakkers and Peters (2011); Zuidema et al. (2001)] and subsequent shish growth, after overcoming a critical flow criterion, to deformation of a mode corresponding to the average molecular weight [Custódio et al. (2009); Swartjes et al. (2003); Zuidema et al. (2001)]. 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 [van Erp et al. (2013)].

Recent experiments using piston driven channel flow have revealed a strong coupling between structure formation and rheology [Ma et al. (2013); Roozemond et al. (2015)]. 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 paper, we present a model that includes all important physical mechanisms 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 [Fernandez-Ballester et al. (2012)], and shish growth rate is taken to be directly proportional to shear rate. Effects of compressibility, nonlinear viscoelasticity, and nonisothermal conditions due to shear heating as well as heat release due to crystallization are all taken into account. 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.

It should be stressed that the purpose of this work was not to develop a predictive model for use in a commercial code. Rather, we attempted to extend a rather well validated phenomenological model for pointlike nucleation toward creation of oriented structures and accompanied viscosity increase to investigate the physics that are at play. Some of the open questions that we have tried to answer are as follows:

- Is there a critical flow criterion that needs to be surpassed before shish appear?
- What determines propagation speeds of shish?
- At what stage in the FIC process does shish start noticeably altering viscosity of the polymer melt?
- What governs Hermans orientation factor, that can be related to mechanical properties [Schrauwen et al. (2004a)]?
II. EXPERIMENTAL

Experiments were conducted using an isotactic polypropylene (iPP) homopolymer (Borealis HD601CF, $M_w = 365$ kg mol$^{-1}$, and $M_n = 68$ kg mol$^{-1}$), also examined in other crystallization studies [Housmans et al. (2009c); van Erp et al. (2012)]. Flow is applied in a confined slit flow geometry within a modified multipass rheometer, by simultaneously moving (in the same direction) the two pistons between which the material is confined. 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 [Ma et al. (2013)]. The reader is referred to this paper for a full description of the experimental setup. Samples were molten at 220 °C for 10 min to erase thermomechanical 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 I. The material near the pistons is kept above the melting temperature to guarantee proper functioning of the pressure transducers.

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 [Portale et al. (2013)] 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 s using a Pilatus 300 K detector. Subsequent isothermal crystallization was monitored in a higher azimuthal range (>90°) using a Frelon detector with an acquisition time of 2.66 s per frame and a total duration of 22 min.

Crystallinity evolution was calculated from the radially integrated patterns as the ratio between the scattered intensity by crystals and the total scatter intensity. The separate crystallization kinetics of the kebab lamellae and the branching lamellae [known as daughters Roozemond et al. (2014)] was determined from the Frelon detector signal. 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 [Dean et al. (1998)]. Examples of procedures for both detectors are given in Fig. 1.

It is important to note that the crystallinity obtained is an apparent crystallinity, because it is an average over the slit thickness. Because the shear rate is maximum at the wall of the channel and zero in the center, crystallinity will progress much faster at the walls than at the center.

Herman’s orientation factor [Hermans et al. (1946); Stein and Norris (1958)] was applied in order to quantify the average level of molecular orientation in the sample.

<table>
<thead>
<tr>
<th>Piston speed (mm/s)</th>
<th>Flow duration (s)</th>
<th>$\dot{\gamma}_w$ (s$^{-1}$)</th>
<th>$\sigma_w$ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>0.25</td>
<td>370</td>
<td>0.121</td>
</tr>
<tr>
<td>80</td>
<td>0.25</td>
<td>500</td>
<td>0.135</td>
</tr>
<tr>
<td>100</td>
<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></td>
<td>0.20</td>
<td>904</td>
<td>0.166</td>
</tr>
</tbody>
</table>
thickness direction and at the location of the diamond window only. The orientation factor is denoted by $f_H$, which is defined as

$$f_H = \frac{3\langle \cos^2 \phi \rangle - 1}{2},$$  

(1)

where $\phi$ is the angle between the crystallographic axis and a reference axis, in this case the flow direction, and $\langle \cos^2 \phi \rangle$ is the average value of the cosine squared of this angle given by

$$\langle \cos^2 \phi \rangle = \frac{\int_0^{\pi/2} I(\phi) \cos^2 \phi \sin \phi d\phi}{\int_0^{\pi/2} I(\phi) \sin \phi d\phi}. 

(2)

The orientation factor $f_H$ is zero for a fully random orientation, and 1.0 or $-0.5$ for a sample fully oriented parallel and perpendicular to the machine direction, respectively. Orientation functions for the b- and c-axis, $f_b$ and $f_c$, were extracted from the baseline subtracted (110) and (040) reflections, taken from the Frelon recorded 2D wide angle x-ray diffraction (WAXD) patterns. Since only very small levels of $\gamma$ and $\beta$ crystals were detected, it is assumed all reflected intensity originated from monoclinic $\alpha$-crystals.

Defining the angles $\epsilon$ and $\sigma$, respectively, the b- and c-axis with the flow direction, and assuming rotational symmetry of all oriented structures, the orientation functions were obtained according to Eq. (1) with

$$\langle \cos^2 \epsilon \rangle = \langle \cos^2 \phi_{040} \rangle, 

(3)

\langle \cos^2 \sigma \rangle = 1 - 0.901 \cdot \langle \cos^2 \phi_{040} \rangle - 1.099 \cdot \langle \cos^2 \phi_{110} \rangle, 

(4)

where $\langle \cos^2 \sigma \rangle$ was calculated using Wilchinsky’s method [Wilchinsky (1960)].

III. MODEL

The model presented in this section is solved numerically in two dimensions with an in-house finite element method (FEM) code. The material confined between the two
pistons is tracked using a moving mesh. The left boundary corresponds to the driving piston. The right boundary corresponds to the material boundary near the comoving piston. The motion of the other nodes moves accordingly with a linear dependence. The Arbitrary Lagrangian Eulerian (ALE) formulation [Hirt et al. (1974)] is employed to take the moving mesh into account. Note that compressibility plays a role and therefore the motion of the left and right material boundary is different during flow start-up, hence stretching and compressing the mesh in flow direction. The governing equations are solved sequentially per time step with semi-implicit Euler time stepping, and a semi-implicit formulation of the stress in the momentum balance [D’Avino and Hulsen (2010)]. A number of stabilization techniques were employed; discrete elastic-viscoelastic stress split (DEVSS) [Bogaards et al. (2002); Guenette and Fortin (1995)], streamline-upwind Petrov–Galerkin (SUPG) [Brooks and Hughes (1982)], and log-conformation representation (LCR) [Hulsen et al. (2005)]. Details about the mesh size and time step are given in Appendix C.

A. Geometry

Figure 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 \( \Gamma_7 - \Gamma_9 - \Gamma_4 \) and \( \Gamma_2 - \Gamma_8 - \Gamma_5 \), and \( T = 145 \) °C on \( \Gamma_6 \).

![FIG. 2. Geometry of the MPR. The graph below indicates the initial condition for the temperature.](image-url)
B. Momentum balance

The momentum balance is given by

$$
\rho(p) \frac{Du}{Dt} = -\nabla p + \nabla \cdot \tau + \nabla \cdot (2\eta(D)),
$$

(5)

where $u$ is velocity and $\rho$ is the density of the material which depends on the pressure $p$ according to Eq. (9). The material derivative $(Du/Dt) = [(\partial u/\partial t) + u \cdot \nabla u]$. A viscous component with viscosity $\eta = 10^{-2}$ Pa s is added for numerical reasons. The deformation rate tensor is denoted by $D$. The extra stress is given by

$$
\tau = \sum_i G_i(c_i - 1),
$$

(6)

with $c_i$ the conformation tensor of mode $i$, calculated with the extended pom-pom (XPP) viscoelastic model [Verbeeten et al. (2004)] (see Sec. III C 1).

1. Boundary and initial conditions

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

- $u = 0$ for all $x$.
  - On the driving piston, the velocity is prescribed
    - $u_x = v_{piston}$, 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
    - $u = 0$, 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; the velocity at the wall is equal to the piston speed at the pistons and goes linearly to zero in 4 mm. At the comoving piston, we define a zero force constraint
    - $F = 0$, on $\Gamma_3$.

Hence, the material does not stick to the comoving 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 is equal to the velocity of the driving piston but grows to this steady state with a time scale governed by compressibility effects.

C. Constitutive modeling

1. Viscoelastic fluid model

The rheological behavior of the material is modeled using the multimode 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 [Verbeeten et al. (2004)]. The conformation tensor is given by

$$
\mathbf{c}_i + 2 \exp\left[\nu_i \left(\sqrt{\text{tr} \mathbf{c}_i / 3} - 1\right) \right] \left(1 - \frac{3}{\text{tr} \mathbf{c}_i} \right) \mathbf{c}_i + \frac{1}{\lambda_{s,i}} \left(\frac{3\mathbf{c}_i}{\text{tr} \mathbf{c}_i} - \mathbf{I}\right) = 0.
$$

(7)
where $\overline{\nabla}$ 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 $\nu_i = 0.1/q_i$ [Verbeeten et al. (2004)]. The Giesekus $\alpha$-parameter is set to 0. The backbone stretch, used in the crystallization model to calculate nucleation density, is given by

$$\Lambda_i = \sqrt{\langle \text{tr} \epsilon_i \rangle / 3}.$$  \hspace{1cm} (8)

The linear viscoelastic spectrum of the iPP used in this study, obtained from small angle oscillatory shear (SAOS) measurements, is given in Table II (i = 2–7). 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 [Roozemond et al. (2011); Steenbakkers and Peters (2011)]. The relation $\lambda_{s,i} \approx \lambda_{b,i}/4$ has been observed for several other polydisperse linear polymer melts [Verbeeten et al. (2004)]. Therefore, we take $\lambda_{s,i} \approx \lambda_{b,i}/4$ and $q = 1$ for all modes except for the mode with the longest relaxation time. For the latter, the parameters were obtained from a fit to uniaxial extensional viscosity data [Roozemond et al. (2011)]. 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 II. To capture steady state pressure drop values it was necessary to add an additional mode with low relaxation time (mode 1 in Table II), 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 bars gives an increase of a factor 1.38 in relaxation times [van Erp et al. (2013)], 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 $E_a = 40 \text{ kJ/mol}$.

2. Compressibility

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

<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>$5 \times 10^{-5}$</td>
<td>$2 \times 10^{-5}$</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>131</td>
<td>0.0014</td>
<td>$3.5 \times 10^{-4}$</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>303</td>
<td>0.011</td>
<td>$2.7 \times 10^{-3}$</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>480</td>
<td>0.060</td>
<td>$1.5 \times 10^{-2}$</td>
<td>1</td>
</tr>
<tr>
<td>5</td>
<td>377</td>
<td>0.29</td>
<td>$7.3 \times 10^{-2}$</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 II. Linear viscoelastic spectrum at $T_{ref} = 220^\circ$C.
\[ p = p_0 - K \ln J, \]  

(9)

where \( p \) is pressure, \( p_0 \) is initial pressure, \( K \) is compression modulus, and the Jacobian \( J = \text{det} \mathbf{F} \) with \( \mathbf{F} \) 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 \( K = 10^9 \text{Pa} \) \cite{van der Beek2005, Zoller1979}.

D. 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

\[ \rho_k c_{p,k} \frac{D T}{D t} = \lambda_k \nabla^2 T + \rho_k \chi_\infty \Delta H \frac{\dot{\varepsilon}}{\dot{\varepsilon}} + \sigma : \mathbf{D}, \]  

(10)

where subscript \( k \) denotes polymer or steel. Values of parameters are given in Table III. The first term in the right hand side represents heat conduction, the second term latent heat release due to crystallization [Eq. (27)], and the third term shear heating, with stress calculated from the XPP model [Eq. (7)]. 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 \cite{Venerus1999}, 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 \cite{Venerus1999}, we trust this is a reasonable approximation.

1. Boundary and initial conditions

The initial condition for the temperature is shown in Fig. 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,

- \( T = 220 \text{°C} \) on \( \Gamma_4 - \Gamma_9 \) and on \( \Gamma_2 - \Gamma_8 \).
- On the centerline, we have \( \frac{dT}{dy} = 0 \), on \( \Gamma_2 \).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value (unit)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (polymer)</td>
<td>( \rho_p )</td>
<td>800 kg/m(^3)</td>
<td>Custódio et al. (2009)</td>
</tr>
<tr>
<td>Heat capacity (polymer)</td>
<td>( c_{p,p} )</td>
<td>3157 J/kgK</td>
<td>Custódio et al. (2009)</td>
</tr>
<tr>
<td>Heat conduction coefficient (polymer)</td>
<td>( \lambda_p )</td>
<td>0.11 W/mK</td>
<td>Custódio et al. (2009)</td>
</tr>
<tr>
<td>Final crystallinity</td>
<td>( \chi_\infty )</td>
<td>65%</td>
<td>Somani et al. (2005)</td>
</tr>
<tr>
<td>Heat of crystallization</td>
<td>( \Delta H )</td>
<td>207 J/g</td>
<td>Custódio et al. (2009)</td>
</tr>
<tr>
<td>Density (steel)</td>
<td>( \rho_s )</td>
<td>8000 kg/m(^3)</td>
<td>Incropera et al. (2007)</td>
</tr>
<tr>
<td>Heat capacity (steel)</td>
<td>( c_{p,s} )</td>
<td>670 J/kgK</td>
<td>Incropera et al. (2007)</td>
</tr>
<tr>
<td>Heat conduction coefficient (steel)</td>
<td>( \lambda_s )</td>
<td>80 W/mK</td>
<td>Incropera et al. (2007)</td>
</tr>
</tbody>
</table>
And on the horizontal line coinciding with the thermocouples in the metal part, we prescribe

- $T = 220{\degree}C$ on $\Gamma_5$, $\Gamma_7$,
- $T = 145{\degree}C$ on $\Gamma_6$.
- The temperature varies linearly in position from 220 to 145{\degree}C on the ceramic rings.

### E. Structure formation

Extensive research in the past decade into the phenomenon of FIC has indicated that flow-enhanced pointlike nucleation is dominated by the chains on the high end of the molecular weight distribution [Roozemand and Peters (2013); Steenbakkers and Peters (2011); van Meerveld et al. (2004)]. Similar to the approach taken by Custódio et al. (2009), Roozemand and Peters (2013), Steenbakkers and Peters (2011), and van Erp et al. (2012), the creation rate of pointlike nuclei is coupled in a phenomenological way to the momentary stretch in the high molecular weight tail of the material (corresponding to the mode having the longest relaxation time, mode 7 in Table II) on a continuum level

$$\frac{DN_f}{Dt} = g_n(T,p)exp(\mu_n(\Lambda_{hmw}^2 - 1)).$$

(11)

where $\Lambda_{hmw}$ is the backbone stretch calculated using the XPP constitutive model [Verbeeten et al. (2004)], and $\mu_n$ and $g_n$ are scaling parameters, the latter of which depends on temperature and pressure following

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

(12)

All parameters in the above equations are given in Table IV. The characterization of this model is elaborated in Appendix A.

The growth mechanism in our model (see Fig. 3) is based on the “streamers” concept proposed by the Kornfield group [Fernandez-Ballester et al. (2012)]. 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 Hwang et al. (2004)], we can assume that the material deforms affinely. We can then express the lengthwise propagation speed of a shish as

$$\dot{L} = \frac{\dot{\varepsilon}_f}{\xi_{seg}}.$$  

(13)

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

### Table IV. Parameters for the flow-induced nucleation model at reference temperature of 166{\degree}C and reference pressure of 100 bars.

<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>m$^{-3}$ s$^{-1}$</td>
</tr>
<tr>
<td>$c_{n,T}$</td>
<td>-0.016</td>
<td>°C$^{-1}$</td>
</tr>
<tr>
<td>$c_{n,p}$</td>
<td>$7.58 \times 10^{-4}$</td>
<td>bar$^{-1}$</td>
</tr>
<tr>
<td>$\mu_n$</td>
<td>0.03</td>
<td>-</td>
</tr>
</tbody>
</table>
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 $\dot{N}_f$ and propagation rate $L$ 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 which is coupled to backbone stretch in the high-molecular weight tail.

It has been observed that shish strongly influence the rheology of the melt before the crystalline volume fraction reaches considerable proportions [Roozemond et al. (2015)]. Chains protruding from the shish into the melt, so-called “hairs” [Hill and Keller (1981); Keller and Kolnaar (1997)], were hypothesized to influence the rheology on a macroscopic scale. This is implemented in an empirical way. The dynamic viscosity as a function of space filling is accurately described by the simple equation [Roozemond (2014); Steenbakkers and Peters (2008)]

$$\frac{DL_{\text{tot}}}{Dt} = 2N_f \gamma \dot{\gamma}, \quad (14)$$

where

$$\frac{\log_{10} \left( \frac{\eta^*|_{\zeta = 1, \omega}}{\eta^*|_{\zeta = 0, \omega}} \right)}{\log_{10} \left( \mu(\omega) \right)} = \xi, \quad (15)$$

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 Roozemond (2014) and Steenbakkers and Peters (2008) crystallized in quiescent conditions, yielding spherulites, whereas for the experimental conditions used here the material will crystallize in highly oriented, more elongated structures. Second, the approach was validated only for SAOS, whereas in this case 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 nonlinear viscoelasticity; not only the viscosity is affected, but we also expect shear-thinning behavior to be affected by this more solidlike phase [Moigne et al. (2013)]. 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, requiring the least adjustable parameters, is to adjust the viscosity of the material via the modulus. Therefore, following Pogodina et al. (1999), we express the moduli of the material as

![FIG. 3. Schematic depiction of segment addition to a shish.](image-url)
Here, \( G_{0,i} \) is the modulus of mode \( i \) in the molten state as given in Table II, and \( \mu \) is the ratio between moduli of crystal and melt, typically for iPP \( \mu = 10^4 \) [Housmans et al. (2009c)]. Finally, \( \nu_{\text{eff}} \) is the effective space filling of shish-kebabs, taking into account their hairy nature, given by

\[
\nu_{\text{eff}} = 1 - \exp\left(-\pi L_{\text{rot}} r_{\text{eff}}^2\right),
\]

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 [Ballard et al. (1978)].

### F. Crystallization kinetics

Due to the speed at which crystallization progresses in the conditions of interest, the heat released during crystallization can not 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 [van Drongelen et al. (2012)]

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

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

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

With \( p \) pressure in bar, \( p_0 \) the reference pressure of 1 bar, and \( \zeta \) the pressure dependence of the melting temperature, \( \zeta = 27.5 \, \text{°C/kbar} \) [He and Zoller (1994)]. The reference temperature \( T^0_{\text{ref}} \) is given at \( p = 1 \) bar in Table V.

Additionally, as proposed by Roozemond et al. (2014), 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 [Balzano et al. (2014); Kumaraswamy et al. (2004)]. We account for this in the following 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 toward their equilibrium conformation with a timescale \( \lambda_G \). The growth rate of parent lamellae \( G_p \) is given by

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

<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^0_{\text{ref}} )</td>
<td>363 K</td>
</tr>
</tbody>
</table>
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 Roozemond et al. (2014); $\mu_{\text{flow}} = 4$, $\lambda_G = 9$ 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

$$G_d(T) = G_{\text{sph}}(T) = G_q(T). \quad (22)$$

To calculate crystalline volume fraction from the nucleation density, specific shish length, and crystal growth rate, two sets of coupled differential equations are used. The first set, also known as the Schneider rate equations [Jerschow and Janeschitz-Kriegl (1997); Schneider et al. (1988)], describes the evolution of the number density, radius density, area density, and undisturbed volume fraction for spherulites from the measured temperature and pressure dependent nucleation density and crystal growth rate. These equations read

$$\begin{align*}
\frac{D\phi_3}{Dt} &= 8\pi\dot{N} \quad (\phi_3 = 8\pi \dot{N}), \\
\frac{D\phi_2}{Dt} &= G_{\text{sph}} \phi_3 \quad (\phi_2 = R_{\text{tot}}), \\
\frac{D\phi_1}{Dt} &= G_{\text{sph}} \phi_2 \quad (\phi_1 = S_{\text{tot}}), \\
\frac{D\phi_0}{Dt} &= G_{\text{sph}} \phi_1 \quad (\phi_0 = V_{\text{tot}}),
\end{align*} \quad (23)$$

where $G_{\text{sph}}$ is the crystal growth rate as determined from Eq. (19). The flow-induced nucleation rate $\dot{\dot{N}}$ is given by Eq. (11). For the kebabs growing on shish (parents), we have

$$\begin{align*}
\frac{D\psi_{2,p}}{Dt} &= 4\pi \dot{L}_{\text{tot}}, \\
\frac{D\psi_{1,p}}{Dt} &= G_p \psi_{2,p}, \\
\frac{D\psi_{0,p}}{Dt} &= G_p \psi_{1,p},
\end{align*} \quad (24)$$

Here, $L_{\text{tot}}$ denotes the specific shish length given by Eq. (14), $G_p$ 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 [Keller and Kolnaar (1997)] while the radius of a shish-kebab grows up to about 100 nm [cf. Roozemond et al. (2015); Seki et al. (2002)].

Following the model proposed by Roozemond et al. (2014), daughter lamellae nucleate on the surface of the parents.
\[
\frac{D\psi_{0,d}}{Dt} = G_{d} f_{d} \psi_{1,p},
\]  

(25)

where \(\psi_{0,d}\) is the undisturbed volume fraction of daughters. The surface area of parent crystals, \(\psi_{1,p}\), is obtained from Eq. (24). 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 [van Drongelen et al. (2012)]

\[
f_{p} = \frac{G_{p}}{G_{p} + G_{d}},
\]

\[
f_{d} = \frac{G_{d}}{G_{p} + G_{d}} = 1 - f_{p}.
\]

(26)

Even here 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 [Avrami (1939)]

\[
\zeta = 1 - \exp(-\phi_{0} - \psi_{0,p} - \psi_{0,d}),
\]

(27)

where \(\zeta\) is the crystalline volume fraction, or space filling. From Eq. (27) follows that the respective crystallization rates of spherulites, parents, and daughters are given by

\[
\dot{\zeta}_{\text{sph}} = (1 - \zeta) \dot{\phi}_{0},
\]

\[
\dot{\zeta}_{p} = (1 - \zeta) \dot{\psi}_{0,p},
\]

\[
\dot{\zeta}_{d} = (1 - \zeta) \dot{\psi}_{0,d},
\]

(28)

when crystallization is complete, the total space filling \(\zeta = \zeta_{\text{sph}} + \zeta_{p} + \zeta_{d} = 1\). By looking at the individual contributions from the different morphologies, we can quantify the final crystalline structure in terms of morphological composition.

**IV. RESULTS**

In this section, we present results from 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 Sec. II. We compare results from the model presented in this paper with previous simulation work from our group [Custódio et al. (2009); van Erp et al. (2013); Zuidema et al. (2001)]. Finally, results of the model in milder conditions are compared in qualitative terms with experiments from literature.

**A. Compressibility effects**

It is important to realize that in such extreme conditions, compressibility of the polymer melt plays an important role in start-up behavior. This is illustrated in Fig. 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 by, for example, Hatzikiriakos and Dealy (1994). The upturn in pressure drop for higher flow rates is caused by structure formation, which was turned off in these simulations.

B. Interplay between structure formation and rheology

Figure 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 most clearly in the first and fourth column, showing velocity and pressure, respectively. The temperature (not shown in the metal part), presented 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 toward the center.

C. Parameter variation

In Fig. 6, we present simulation results for a flow condition of 100 mm/s for 0.20 s, with varying segment length ξseg. The radius at which shish influence the rheology reff 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 ξseg is the increased shear layer thickness; because shish grow at higher speeds, the modulus increases faster, causing a faster propagation of the shear layer.

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, where the radius at which shish affect rheology reff was varied. For low reff, 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 reff, the modulus of the melt is already increased significantly for shish that are spaced far apart (i.e., low Ltot), causing a fast propagation of the shear layer front but a low total shish density within the layer.
From Figs. 6 and 7, we conclude that a good agreement with experiments is obtained for the parameter set $n_{\text{seg}} = 5\text{ nm}$ and $r_{\text{eff}} = 50\text{ nm}$. 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 [Ballard et al. (1978) 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 [Hwang et al. (2004)], so the macroscopic shear rate might be increased. Moreover, the approach with which the effect of shish on the rheology is calculated [Eq. (17)] does not take the influence of shish on the nonlinear viscoelastic properties into account. Most probably, the shish not only increase the modulus, but also significantly decrease shear thinning behavior [like glass fibers, cf. Moigne et al. (2013)]. 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 shishlike structures on nonlinear viscoelastic properties, possibly based on numerical calculations, is highly desirable. A possible direction for such a model was proposed by Steenbakkers and Peters (2008).

D. Validation with experimental results

The results from the Sec. IV C showed that a good agreement with experiments at a flow condition of 100 mm/s for 0.2 s was obtained for the two adjustable parameters
Using this parameter set, we performed simulations for additional flow condition. Comparison between experiments and simulations are presented in Fig. 8. Simulations capture the experimental data quite accurately, both in terms of pressure drop [Fig. 8(a)] and apparent crystallinity [Fig. 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 Sec. IV E. 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 B, it is shown that the model shows satisfactory agreement with experimental data at much milder flow conditions.

Figure 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.
FIG. 7. (a) Pressure drop, (b) apparent crystallinity, and (c) shish length density at the window, for varying $r_{\text{eff}}$. The segment length is kept constant at $\zeta_{\text{seg}} = 5$ nm. Symbols show experimental data, and lines show results from simulations.

FIG. 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 and (b) apparent crystallinity.
Ultimately, this work is aimed at connecting processing conditions to final properties. Schrauwen et al. (2004a) showed that yield stress was related to orientation of the crystalline phase, expressed in the Hermans’ orientation factor of the c-axis of the unit cell, \( f_c \). From our calculations, we can extract the Hermans’ orientation factor from the volume fractions of parent and daughter crystals; kebabs (parents) have their c-axis oriented parallel to flow direction (i.e., \( f_c = 1 \)), whereas daughter lamellae are oriented at an angle of approximately 80° with respect to flow direction; hence, \( f_c = -0.45 \).

The Hermans’ orientation factor in an oriented crystalline piece of material is therefore given by

\[
f_c = \frac{1 \times \xi_p - 0.45 \xi_d}{\xi_p + \xi_d},
\]

with \( \xi_p \) and \( \xi_d \) the volume fractions of parents and daughters, respectively. The x-ray beam traverses across thickness direction in the present experiments; therefore, we should calculate the average Hermans’ orientation factor over the thickness of the slit at the location of the beam

\[
\langle f_c \rangle = \frac{1}{d} \int_0^d f_c \, dy,
\]

where \( d \) is the thickness of the slit. Experimental and calculated values for the average Hermans’ orientation factor of the c-axis \( \langle f_c \rangle \) are presented in Fig. 10. The final value is captured quite well by our calculations for all flow conditions. An interesting direction for future work would be to investigate if the calculated Hermans’ orientation factor is a good predictor of mechanical properties for this type of material under relevant flow conditions.

Increasing flow time while keeping piston speed constant shows similar trends as increasing the piston speed, as demonstrated in Fig. 11. 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.
E. Shear layer thickness and flow instabilities

Figure 12 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 numerical model no longer converges. The morphology that we show in Fig. 12 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 [Custódio et al. (2009);
Kornfield et al. (2002)]. These are indications that the oscillations are not a numerical artifact, but that the flow actually might become unstable for these conditions.

Because the simulations stop converging at some time during the flow pulse, we cannot 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. 8(a)] is reproduced very well up to the time where oscillations start occurring.

**FIG. 12.** POM 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) Results for piston speed of 60 mm/s and flow time 0.25 s and (b) 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.
F. 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. (2001). The model presented by Zuidema was slightly modified by Steenbakkers and Peters (2011), who replaced the recoverable strain by backbone stretch, and also used by Custódio et al. (2009). 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. (2013) showed that a more realistic critical condition is a cumulative stretch, i.e., time integral over backbone stretch.

The model presented in this paper 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. 13, where we have shown experimental data and simulations with the current model and the most recent formulation of Zuidema’s model [van Erp et al. (2013)] 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 14(a) shows the nucleation density after flow as a function of position along the slit. For Zuidema’s model, the maximum value is around $10^{14}$ 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 $\approx 10^{20}$ m$^{-3}$. The specific shish length is around $10^{13}$ m/m$^3$ [cf. Fig. 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. Barham and Keller (1985)]. This length of $\approx 100$ nm might correspond to the size of each of the crystalline blocks.

![FIG. 13. 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, and dashed lines show Zuidema’s model (van Erp et al. (2013)).](image-url)
Figure 14(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 by van Erp et al. (2013). The critical value that van Erp et al. (2013) 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 paper. It is for this reason that we have chosen to modify Zuidema’s model in the way presented here. The current model also captures experimental data in milder flow conditions, as demonstrated in Sec. IV G and Appendix B.

G. Structure formation at lower flow rates

The results presented so far 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 MPa for the experiments presented in this paper), revealed qualitatively different results. For example, Fernandez-Ballester et al. (2012) found a less oriented type of morphology [Kornfield et al. (2002), 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 before sections. The adjustable parameters are again set to $\delta_{\text{seg}} = 5 \text{nm}$ and $r_{\text{eff}} = 50 \text{nm}$. Figure 15 shows the calculated nucleation density and specific shish length after flow for 1 s and subsequent crystallization at 145 °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 $\approx 10 \mu\text{m}$ [Eder and Janeschitz-Kriegl (1997)]. Consequently, the fraction of crystal structure that is isotropic is much larger than the oriented crystal fraction (see Fig. 16). 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.
For the flow condition with $v_{piston} = 30$ 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/m$^3$, corresponding to inter-shish distance between $\approx 750$ and 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 [Fernandez-Ballester et al. (2012)]. Hence, this value indicates a sausagelike 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.

V. CONCLUSIONS

We have presented a detailed model for FIC 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 crystalline volume fractions.

FIG. 15. Nucleation and shish length densities for simulations with flow time of 1 s and varying piston speed.

For the flow condition with $v_{piston} = 30$ 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/m$^3$, corresponding to inter-shish distance between $\approx 750$ and 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 [Fernandez-Ballester et al. (2012)]. Hence, this value indicates a sausagelike 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.

FIG. 16. 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, 0.087, and 0.095 MPa.

FIG. 16. 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, 0.087, and 0.095 MPa.
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.

Coming back to the questions that were posed in the introduction, the following conclusions can be stated:

- Crystalline morphologies created in both in low and high shear rate regimes can be modeled without posing a critical flow criterion for the formation of shish.
- Propagation speeds of shish can be linked to shear rate and are in the order of $\mu$m/s.
- Shish significantly affect the melt viscosity at very low levels of space filling (in the order of 1%), indicating that noncrystalline material (possibly in the form of chains tethered to shish) plays a crucial role.
- The Hermans orientation factor is a result from different crystal orientations (parent and daughter lamellae) growing on shish.

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.

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APPENDIX A: CHARACTERIZATION OF FLOW-INDUCED NUCLEATION

To determine all parameters for the flow-induced nucleation model [Eq. (11)], we used the experimental data set that was presented by van Erp et al. (2012, 2013). The experiments were performed in the Pirouette extended dilatometer [Housmans et al. (2009a); van Erp et al. (2012, 2013)]; 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$ bars). A shear pulse with 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 the Clapeyron equation [He and Zoller (1994)]. The specific volume of the material was monitored. The experimental crystallization temperature was defined as shown in Fig. 17, which corresponds to a space filling of $\sim$10% [van Erp et al. (2013)]. The Schneider rate equations (Sec. III F) were used to calculate crystallization kinetics during cooling. The crystallization temperature from calculations was defined at the temperature where $\xi = 0.12$.

Experiments and calculations are compared in terms of dimensionless transition temperature $\Theta$ as
with $T_{cQ}$ the crystallization temperature in quiescent conditions and $T_{c}^{\gamma}$ the crystallization temperature after shear. Hence, $\Theta = 1$ if shear has no effect and $\Theta$ increases with shear rate. 

Van Erp et al. (2012, 2013) determined the critical shear rate for appearance of oriented crystalline structures from small angle x-ray scattering (SAXS). Generally, the morphology was isotropic for shear rates up to 100 and 30 s$^{-1}$ for undercoolings of 30 and 60 $^\circ$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

$$\dot{N}_f = g_n(T, p) \exp (\mu_n(A_{hmw}^2 - 1)), \quad (A2)$$

where the pressure and temperature dependence of $g_n$ is given by

$$g_n(T, p) = g_n^{ref} 10^{\kappa_n(T-T_{ref}) + \chi_n(p-p_{ref})}. \quad (A3)$$

FIG. 17. Method of determining crystallization temperature from dilatometry experiments.

FIG. 18. Dimensionless crystallization temperature versus shear rate corrected for temperature and pressure for (a) undercooling of 30 $^\circ$C (i.e., $T_{shear} = 167 ^\circ$C at 100 bars) and (b) undercooling of 60 $^\circ$C (i.e., $T_{shear} = 137 ^\circ$C at 100 bars). Open symbols show measurements, closed symbols show calculations.
Hence, we need to determine four parameters to fully characterize the flow-induced nucleation; $l_n$, $g_{n,\text{ref}}$, $c_{n,T}$, and $c_{n,p}$. To achieve this, the fitting is performed in three steps:

1. First, $l_n$ and $g_{n,\text{ref}}$ are determined from the experiments with $\Delta T_f = 30{\degree}C$ and $p = 100$ bars.
2. Second, $c_{n,T}$ is determined from the experiments with $\Delta T_f = 60{\degree}C$ and $p = 100$ bars.
3. Third, we determined $c_{n,p}$ from the experiments with $\Delta T_f = 30$, $60{\degree}C$, and $p = 500$, $900$, and 1200 bars.

The resulting parameters are given in Table IV. The calculations with these parameters are compared with experimental data in Fig. 18. The experimental data and calculations show a good agreement, indicating that for these conditions, the presented model gives an accurate representation of flow-induced nucleation.

**FIG. 19.** Dimensionless crystallization temperature versus shear rate corrected for temperature and pressure for flow at (a) undercooling of $30{\degree}C$ (i.e., $T_{\text{shear}} = 167{\degree}C$ at 100 bars) and (b) undercooling of $60{\degree}C$ (i.e., $T_{\text{shear}} = 137{\degree}C$ at 100 bars). Open symbols show measurements, and closed symbols show calculations. Black symbols indicate isotropic final morphology (determined using SAXS), and gray symbols indicate oriented final morphology. It is important to note that $\Theta$ levels off at high shear rates for $\Delta T_f = 60{\degree}C$ because the crystallization temperature becomes equal to the flow temperature.

**FIG. 20.** Time step convergence.
APPENDIX B: VALIDATION OF SHISH GROWTH MODEL WITH PIROUETTE DATA

In Appendix A, the experimental data set obtained in the Pirouette dilatometer (at low to mild shear rates) from van Erp et al. (2012, 2013) was used to calibrate our flow-induced nucleation model. Based on recent experimental evidence [Roozemond et al. (2015)], in this paper, we proposed an improved model for shish propagation, which was validated using channel flow experiments. In this Appendix, we compare calculations with the improved shish propagation 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 19 shows experimental data and calculations for these experiments. The black symbols indicate experiments where the final morphology was isotropic, and 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.

APPENDIX C: MESH AND TIMESTEP CONVERGENCE

Figure 20 depicts the evolution of pressure drop for different time step sizes. Mesh convergence is presented in Fig. 21. Based on these results, we have performed all simulations, unless noted otherwise, with a mesh of $50 \times 20$ elements in x–y direction and a time step of $10^{-5}$. These values give sufficiently accurate results at relatively low computational expansiveness.

References

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