Saturated Nucleation and the Classification Problem in Flow-Induced Crystallization of Polymers

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Introduction
The first step towards ‘processing for properties’ of semicrystalline polymers is to characterize morphological regimes in terms of flow conditions. A study of flow-enhanced nucleation (FEN) sheds new light on a recently proposed classification, based on characteristic Weissenberg numbers, Wt [1].

Experiments
Flow-induced crystallization (FIC) of isotactic poly-1-butene (Basell PB0400) was studied by in situ microscopy in a shear cell (Linkam CSS 450). Samples were annealed at T = 200°C for 10 minutes to erase residual structure, cooled to T = Tc at 10°C/min, then sheared (rate γ, time t). Fibrils, oriented in the flow direction, were formed at high γ and overgrown by spherulites in the relaxed melt (Fig. 1, bottom). Spherulitic FEN at low γ (top, middle) will be simulated numerically.

Modeling
Flow-induced precursors and nuclei are formed until their number density, Npf + Nnf, saturates at Nf,max:

\[ \dot{N}_{pf} + \dot{N}_{nf} = g_p T(B_c) \left[ 1 - \frac{N_{pf} + N_{nf}}{N_{f,max}} \right] \]

in which B_c is the recoverable strain, \( \lambda \) the stretch, and S the orientation of long chains, from a single-mode Rolie-Poly model [3] with reptation and stretch relaxation times

\[ \lambda_{rep} = \lambda_0 \left[ 1 + a N_{pf} \right] ; \quad \lambda_{str} = \lambda_0 \left[ 1 + a N_{pf} \right] \cdot \]

\[ T = T_1 = J_2(S^4), \quad T = T_2 = \Lambda^4 - 1, \quad \text{and} \quad T = T_3 = J_2(B_c^2) \]

are tested; \( d \) signifies the deviatoric part of a tensor. Nuclei, which crystallize, are modeled as growing soft particles [4].

Results
Saturation levels, from the data in Figs. 2a-b, are plotted versus Wi,t = \( \lambda_{rep} \) and Wi,rep = \( \lambda_{str} \) in Fig. 2c. The model is fitted to the data for \( \dot{\gamma} = 1s^{-1} \). To explain the narrow size distribution of spherulites, we let \( \tau_{pn} \) go from infinity to zero at \( t = t_0 \); \( N_{pf} \) and \( N_{nf} \) then vanish. Since Wi,t > 1 correlates with significant FEN, the obvious choice for \( I \) is \( I_1 \). However, contrary to the data, a lower nucleation density is predicted for higher \( \dot{\gamma} \) and shorter \( t \). Results with \( I_2 \) and \( I_3 \) are nearly equal and in excellent agreement with the data, except for \( \dot{\gamma} = 10s^{-1} \) at \( T_c = 98°C \), where the model does not apply because fibrils were formed.

![Figure 1: Morphology evolution at T_c = 93°C. Top: quiescent. Middle: \( \dot{\gamma} = 1s^{-1} \) and \( t_s = 10s \). Bottom: \( \dot{\gamma} = 10s^{-1} \) and \( t_s = 1s \). The bar measures 100um. From [2].](image)

![Figure 2: (a) Open symbols: spherulitic nucleation density at T_c = 93°C. Lines with filled symbols: simulation results for different \( I \). (b) Idem at T_c = 98°C. (c) Saturation level versus Wi,t = \( \lambda_{rep} \) and \( Wi_0 = \lambda_{str} \). Colours are explained in the Table.](image)

<table>
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<th>( \dot{\gamma}[s^{-1}] )</th>
<th>0.01</th>
<th>0.1</th>
<th>1</th>
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<td>( Wi_0 [s] )</td>
<td>9.8</td>
<td>9.3</td>
<td>10</td>
<td>10</td>
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<tr>
<td>( \lambda_{rep} [s] )</td>
<td>0.1</td>
<td>0.04</td>
<td>0.07</td>
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Table: Nominal melting temperature \( T_m \), initial reptation and stretch relaxation times of the long chain fraction [6], experimental conditions, and fit parameters.

Conclusions
- The flow-enhanced nucleation density saturates. If oriented fibrils grow from pointlike precursors, saturation of their average lateral spacing [7] is not surprising.
- Chains must be stretched by the flow. Depletion of sufficiently long chains explains the saturation process.
- Creation of a few precursors due to minor chain stretch, when Wi,rep < 1, can lead to Wi,rep (t < t_s) >> 1: Classification of FIC experiments is limited to short flows.
- Different values of \( g_p \) and \( a \) have been obtained for different temperatures (Table). This was unexpected and requires further investigation.

References: