

Temperature effects on saturation of flow-enhanced nucleation

Citation for published version (APA):

Steenbakkens, R. J. A., Peters, G. W. M., Baert, J., & Puyvelde, van, P. C. J. (2008). *Temperature effects on saturation of flow-enhanced nucleation*. Poster session presented at Mate Poster Award 2008 : 13th Annual Poster Contest.

Document status and date:

Published: 01/01/2008

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

Temperature Effects on Saturation of Flow-Enhanced Nucleation

R.J.A. Steenbakkers and G.W.M. Peters¹
J. Baert and P. van Puyvelde²

1. Polymer Technology, TU Eindhoven
2. Chemical Engineering, KU Leuven

Introduction

In melt-processing of semicrystalline polymers, flow-induced crystallization is inevitable. Understanding of this phenomenon is required for process optimization. *Flow-enhanced nucleation (FEN)* is considered here.

Model of FEN kinetics

The nucleation rate depends on the number of quiescent and *flow-induced precursors (FIPs)* available:

$$\dot{N}_n = \dot{N}_{nq} + \dot{N}_{nf} = \frac{N_{pq} + N_{pf}}{\tau_{pn}}$$

Pointlike FIPs form due to stretch of long chains, Λ :

$$\dot{N}_{pf} = g_p (\Lambda^4 - 1) \left(1 - \frac{N_{pf} + N_{nf}}{N_{f,max}} \right) - \dot{N}_{nf}$$

The number of FIPs and flow-induced nuclei saturates at $N_{f,max}$. The reptation time and Rouse time of the slowest relaxation mode change proportional to the number of FIPs ('branching' of long chains). Crystallites, growing from nuclei, behave like viscoelastic particles.¹

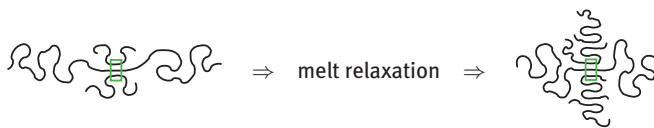


Figure 1: FIP formation on a stretched chain and nucleation after flow.

Experiments (Linkam shear cell)

Isotactic poly-1-butene ($\bar{M}_w = 176 \text{ kg mol}^{-1}$, $\bar{M}_w/\bar{M}_n = 5.7^2$) was sheared, varying the rate $\dot{\gamma}$ and strain $\dot{\gamma}t_s$, after cooling to different temperatures (Table 1, Figure 2).

Table 1: Experimental conditions and initial longest relaxation times.

T_m [°C] ²		$\dot{\gamma}$ [s ⁻¹]			λ_0^{rep} [s] ²	λ_0^{R} [s] ²
110.7		△	□	▽		
T [°C]	93	0.1	1	5	4.92	0.17
	98	0.1	1	10	3.99	0.14
	103	1	5	10	3.26	0.11

In situ microscopy showed mainly spherulites, but none during flow, even after the time when they appeared in the quiescent melt. Hence $\tau_{pn} (\dot{\gamma} > 0) \gg t_s$: FIPs nucleate only if the melt relaxes (Figure 1). The distribution of spherulite radii was narrow, thus $\tau_{pn} (\dot{\gamma} = 0) \rightarrow 0$.

Results

Using the Rolie-Poly model³ to calculate Λ , FEN data are reproduced well, except for short fast flows (Figure 2). The parameter g_p scales with the rheological shift factor:

$$g_p(T) = a_T(T, T_{ref}) g_{p,ref}$$

The saturation limit, taken from the data, shows a quadratic dependence on $Wi = \dot{\gamma} \lambda_0$ at low temperature and a 4th-power dependence at high temperature.

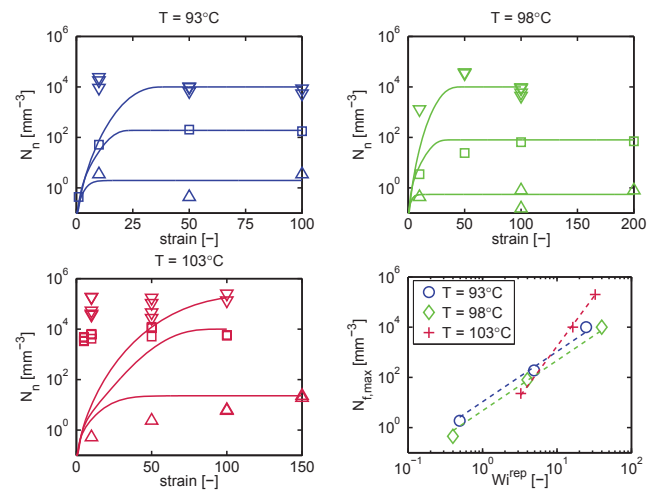


Figure 2: FEN and its saturation at different temperatures.

Conclusion

Higher temperature lowers the stretch-sensitivity of FEN via a_T (chain mobility) but increases the saturation limit. This unexpected result is a subject of current research.

References

- [1] R.J.A. Steenbakkers and G.W.M. Peters, *Suspension-based rheological modeling of crystallizing polymer melts*, Rheol. Acta 47 (2008)
- [2] J. Baert et al, *Flow-induced crystallization of PB-1: from the low shear rate region up to processing rates*, Macromolecules 39 (2006)
- [3] A.E. Likhtman and R.S. Graham, *Simple constitutive equation for linear polymer melts derived from molecular theory: Rolie-Poly equation*, J. Non-Newtonian Fluid Mech. 114 (2003)