Temperature effects on saturation of flow-enhanced nucleation

Technische Universiteit **Eindhoven** University of Technology

Temperature Effects on Saturation of Flow-Enhanced Nucleation

R.J.A. Steenbakkers and G.W.M. Peters[1]
J. Baert and P. van Puyvelde[2]

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:

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

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 ($\bar{M}_w = 176\,\mathrm{kg\,mol^{-1}}$, $\bar{M}_w/\bar{M}_n = 5.7$[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 $\tau_{pn}(\dot{\gamma} = 0) \to 0$.

Results

Using the Rolie-Poly model[3] 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 $\mathrm{Wi} = \dot{\gamma}\lambda_0$ at low temperature and a 4$^{\mathrm{th}}$-power dependence at high temperature.

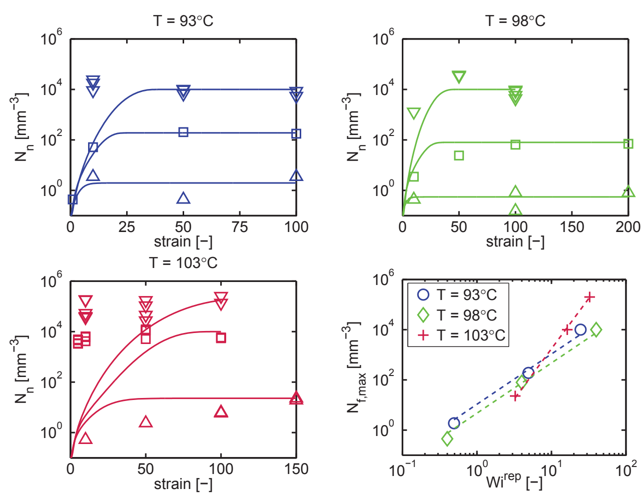

Figure 2: FEN and its saturation at different temperatures.

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)