Modeling flow-induced crystallization of polymers

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Modeling Flow-Induced Crystallization of Polymers

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Introduction

A framework for modeling flow-induced crystallization of polymers is being developed. The effect of crystallites on the rheology of the melt is accounted for by a suspension model. The flow-induced crystallization kinetics are described by a model for the creation and growth of (unstable) precursors and their transformation into (stable) nuclei.

Modeling

Suspension rheology

In the linear viscoelastic regime the dynamic modulus is written as

$$G^* = f_G^*\left(\xi_g, G_0^*, G_1^*, \ldots\right) G_0^* \,. \tag{1}$$

We use the generalized self-consistent method (GSCM [1]) to calculate the relative dynamic modulus f_G^* from the space filling ξ_g. The results are compared to a widely used scaling law,

$$G' = \left[G_1' - G_0'\right] \xi_g + G_0' \,, \tag{2}$$

for the storage modulus. An extension to nonlinear viscoelastic behavior is currently being made.

Flow-induced crystallization kinetics

The rate of change of the number of precursors is given by the evolution equation

$$\dot{N}_p = I_p + \dot{T}\frac{\partial N_{pa}}{\partial T} - \frac{N_p}{\tau_{pd}} - \frac{N_p}{\tau_{pn}} \tag{3}$$

with the nucleation rate

$$\dot{N}_n = \frac{N_p}{\tau_{pn}} \,. \tag{4}$$

The rheology of the melt is described by the eXtended Pom-Pom (XPP) model. We use a modified Zuidema model [2] for the rate of sporadic creation of precursors,

$$I_p = \tilde{g}_p \left(\Lambda^4 - 1\right) \,, \tag{5}$$

where $\Lambda = \sqrt{\mathrm{tr}(\boldsymbol{B}_e)/3}$ is the backbone stretch of the highest relaxation mode. The 'branching' parameter q of the XPP model is related to the number of flow-induced precursors as

$$q = q_0 \left[1 + a N_{pf}\right] \,. \tag{6}$$

A depletion of molecules long enough to form precursors [3] is incorporated in $\tilde{g}_p$. Furthermore, we assume that flow inhibits nucleation. A simple step function, where τ_{pn} jumps from infinity to zero as the flow is switched off, suffices for the experiments used here. Growth of pointlike precursors into threadlike precursors is also modeled, but this part has not been validated by experiments yet.

Validation

In figure 1 the storage modulus, calculated from the experimentally determined ξ_g, G_0^* and G_1^*, is compared to the storage modulus measured after short-term shearing of a linear isotactic polypropylene (iPP) melt at $135°$C.

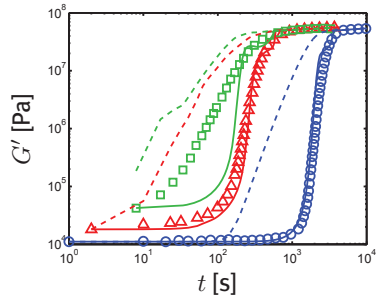

Figure 1. *Evolution of the storage modulus after shearing at $\dot{\gamma} = 60\mathrm{s}^{-1}$ for $t_s = 0\mathrm{s}$ (○), $3\mathrm{s}$ (△), and $6\mathrm{s}$ (□), simulated by the linear scaling law (dashed lines) and the GSCM (solid lines).*

Whereas the linear scaling law fails, the GSCM yields good results, except for high shear times (probably due to development of a network structure).
Space filling and nucleation density are predicted quantitatively by the kinetics model for processes where point nucleation dominates, as shown in figure 2 for iPP at $135°$C.

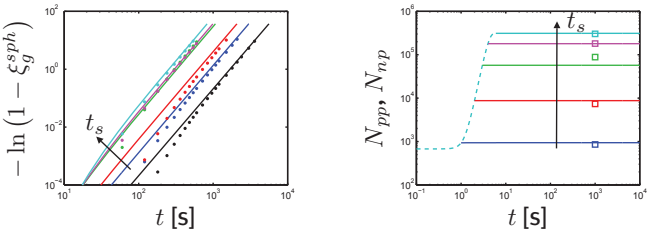

Figure 2. *Left: 'Avrami plot' of space filling due to spherulites. Right: numbers of pointlike precursors (dashed lines) and nuclei (solid lines). Symbols are data for $\dot{\gamma} = 60\mathrm{s}^{-1}$ and different t_s.*

An additional validation is provided by the narrow size distribution of crystallites observed in the experiments, which is captured here due to the assumption that precursors are not nucleated until the flow is switched off.

Conclusions

- Crystallizing polymer melts can be modeled as suspensions. The properties of the phases change due to the evolving microstructure.
- Flow-induced point nucleation is described quantitatively by our model of flow-induced crystallization kinetics.

Future work

- Describe the transition to oriented growth.
- Simulate crystallization during continuous flow.

References:

[1] Christensen, R.M. (J. Mech. Phys. Solids 38, 379–404, 1990)

[2] Zuidema, H.; Peters, G.W.M.; Meijer, H.E.H. (Macromol. Theory Simul. 10, 447–460, 2001)

[3] Somani, R.H.; Hsiao, B.S.; Nogales, A.; Srinivas, S.; Tsou, A.H.; Sics, I.; Balta-Calleja, F.J.; Ezquerra, T.A. (Macromolecules 33, 9385–9394, 2000)

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