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technische universiteit eindhoven

Influence of cooling rate on the PVT-behavior of Semi-Crystalline Polymers

M.H.E. van der Beek, G.W.M. Peters, H.E.H. Meijer

Introduction

PVT-behavior of polymers is one of the main properties determining final product shrinkage, correct modeling of this is essential for control of product dimensions. Although pVT-behavior of semi-crystalline polymers has been the subject of several studies, important parameters such as cooling rate and deformation history have not been studied extensively.

- Objective of this study is to improve the modeling of pVT-behavior of semi-crystalline polymers as a function of cooling rate.

Theory

Crystalline and amorphous phase are assumed to behave as independent components with separate contributions to the specific volume:

$$\rho = \xi\rho_c + (1-\xi)\,\rho_a$$

ρ_a, ρ_c describe the asymptotic high- and low-temperature pVT-behavior of the amorphous and crystalline phase respectively. The degree of crystallinity ξ is used to describe the crystallization transition, calculated via Schneider rate equations / Avrami model:

$$\dot{\phi}_3 = 8\pi\alpha \quad (\phi_3 = 8\pi N) \qquad \text{'rate'}$$
$$\dot{\phi}_2 = G\phi_3 \quad (\phi_2 = 8\pi R_{tot}) \qquad \text{'radius'}$$
$$\dot{\phi}_1 = G\phi_2 \quad (\phi_1 = S_{tot}) \qquad \text{'surface'}$$
$$\dot{\phi}_0 = G\phi_1 \quad (\phi_0 = V_{tot}) \qquad \text{'volume'}$$
$$\phi_0 = -\ln(1-\xi_g) \qquad \text{'space filling'}$$
$$\xi = V_\infty \xi_g) \qquad \text{'crystallinity'}$$

The local crystallinity per spherulite V_∞, nucleation rate N(T) are taken from [1]. The growth rate G(T,p) is also taken from [1] but is modified with respect to pressure dependence:

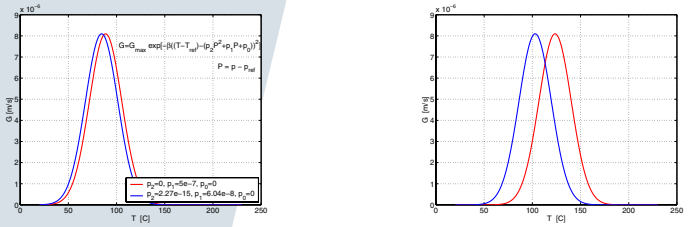

Figure 1. *Modified G(T,p) and G(T,p) according to [1] depicted for pressures 10 [MPa] (left) and 80 [MPa] (right).*

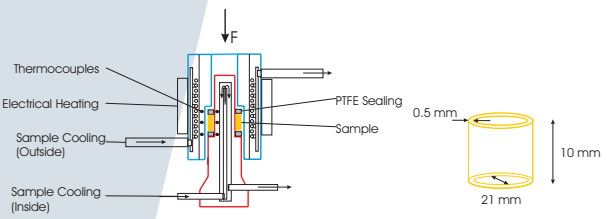

Figure 2. *Schematic representation of the set-up.*

Experimental

The material investigated is an isotactic polypropylene hompolymer supplied by Borealis, grade K2Xmod (Mw = 365000, Mn = 67000). An experimental setup based on the principle of confined compression is used to investigate the influence of cooling rate on pVT-behavior.

Results

The pVT-behavior of the i-PP measured at $\frac{\partial T}{\partial t}_{max}$ = 0.13 [K/s], shows good agreement with asymptotic values gathered from 'equilibrium' pVT data (top left).

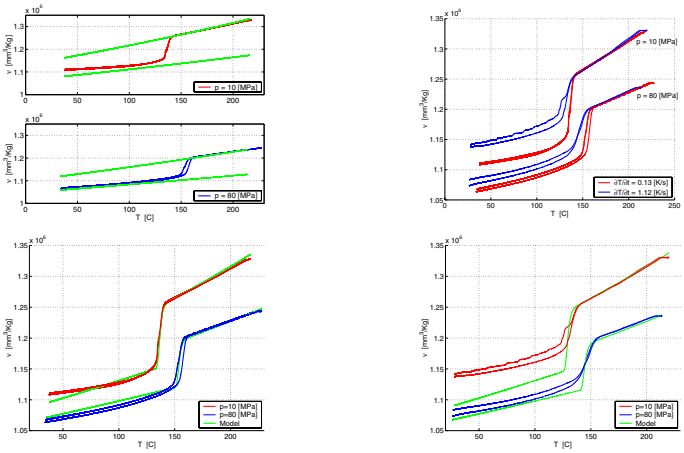

Figure 3. *Calculated and measured pVT-behavior of i-PP at different cooling rates.*

Increasing cooling rate to $\frac{\partial T}{\partial t}_{max}$ = 1.12 [K/s], already introduces differences in onset of crystallization and specific volume in the crystalline phase (top right). Model predictions show good agreement for low cooling rate with respect to onset of crystallization, temperature range of crystallization, and final degree of crystallinity (lower left). However, with increasing cooling rate predictions deviate noticably from pVT data measured at 10 [MPa] (lower right).

Conclusions

- PVT data measured at $\frac{\partial T}{\partial t}_{max}$ = 0.13 [K/s] agree well with asymptotic values derived from 'standard' pVT-measurements
- A 'quadratic' pressure dependence of the growth rate G(T,p) is necessary to capture the pressure dependence of pVT-behavior
- In general, model predictions show good agreement with measured pVT-data. Deviations from measurements at $\frac{\partial T}{\partial t}_{max}$ = 1.12 [K/s] and p = 10 [MPa] have to be investigated further.

References:

[1] Zuidema, H.: *Flow Induced Crystallization of Polymers* (ISBN 90-386-3021-2 , 2000)

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