Measurements on Flow-Induced Crystallization

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Introduction
The resulting properties of semi-crystalline polymer products strongly depend on both molecular properties and the processing conditions applied, i.e. the thermal-mechanical history experienced (see for example Fig. 1). To control the properties, processes (e.g. in injection moulding, film blowing or fiber spinning) have to be modeled in terms of nucleation and crystallization kinetics and their dependence on flow-induced structure formation.

The goal of this work is to provide experimental data to develop and to check constitutive equations.

Figure 1: Different mechanical history/same thermal history. Left: quiescent; Right: after short time shearing at 140 °C

Measurements were performed in shear (rheometer) and elongational flow (cross-slot flow cell) for two different isotactic Polymethylmethacrylates: StamylanP 13E10 (M_w=501 [kg/mol] and MWD=6.0) and 15M10 (M_w=354 [kg/mol] and MWD=5.6).

Shear Flow

Figure 2: Storage modulus, 1 [s] shearing at 140 °C for 13E10 (left) and 15M10 (right).

Figure 3: Enhancement of crystallization after short time shearing at 140 °C for 13E10 (left) and 15M10 (right). Points having the same shear rate are connected with a line.

Elongational Flow

Figure 4: The cross-slot flow cell. Flow is created by moving a ring with two cams. The enlarged detail illustrates the stretching of polymer chains in the hyperbolic flow-field [1].

Figure 5: WAXS intensity of 13E10 vs orientation angle and position for the (110) reflection after applying flow (ε ≈ 0.38 [s^{-1}] for 13:39 minutes) at 148.4 °C on the inflow centerline (left) and on the outflow centerline (right).

Figure 6: Field-wise birefringence measurement on 13E10 (T=144.9 °C and ε ≈ 0.38 [s^{-1}]). Flow direction as given in Figure 4. Left: during flow, three minutes after starting the flow. Middle and right: 4 minutes and 10 minutes after cessation of flow.

Figure 7: Prediction of the space filling in the cross-slot flow cell for Daplen KS10, using the S_n model. Left: plane z=0.05 [mm]. Right: Variation of the space filling in the depth of the cell.

Conclusions
• Molecular properties (M_w and MWD) influence flow-induced nucleation and crystallization (Fig. 2 and 3).
• High oriented structure is found around stagnation point in the cross-slot flow cell (Fig. 5 and 6).
• Qualitative agreement is found between the birefringence and WAXS experiments, and the numerical prediction (Fig. 5, 6 and 7).
• Numerical simulations show large shear gradients in the height and depth of the cross-slot flow cell (Fig. 7).

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References