

Flow-induced crystallisation of polyethylene (PE) and polypropylene (PP) melts



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μPP^2

General abstract

Thermoplastic semi-crystalline polymers are processed by cooling them from the melt and giving shape to the final product during solidification.

In industrial forming processes (such as injection moulding, film blowing or fibre spinning) these materials crystallise from the melt under flow. The final morphology of the crystalline material, which deeply influences the mechanical properties, is highly dependent on the thermo-mechanical history of the crystallising melt.

Understanding Flow-induced Crystallisation (FIC) would allow predicting the final properties of the product as a function of the processing parameters, avoiding the wastage of resources of the current trial-and-error methods.

At present, FIC in complex thermo-mechanical histories is modelled with semi-empirical, material specific models, based on modifications of the Avrami theory of nucleation and growth. The physical understanding is however still limited and the experimental evaluation of the model parameters very difficult.

Technical abstract

This work is part of a systematic series of experiments to better understand and model the physical processes that govern the flow-induced crystallisation of PE and PP.

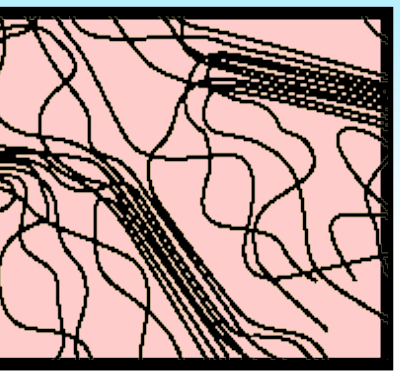
Within the Department of Chemical Engineering at Cambridge, optical and X-ray studies of FIC have been made using a Multi-Pass Rheometer. O.Saquet *et al.* (2001) and G. Hernandez (PhD thesis, 2007) reported experimental observations on the way that flowing polyethylene melts can crystallise within a processing channel geometry.

The Multi-pass Rheometer (MPR) allows to generate well-controlled complex flows that can be numerically simulated. Flow-induced birefringence experiments at the molten state allow to visualise the stress field in the polymer and to validate the constitutive model when no FIC is occurring. Then the simulations can be used to identify the stress, orientation, stretch of the polymer chains in the regions of localised crystal formation in the FIC experiments. That should lead to the identification of the physical phenomena at the basis of Flow-Induced Crystallisation.

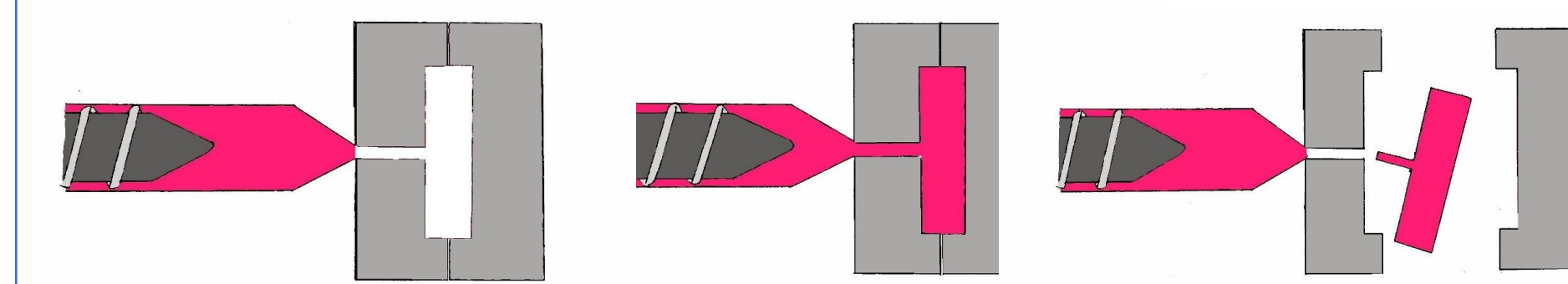
Glossary:

Semi-crystalline polymers:

Polymers that at the solid state show an alternance of amorphous and crystalline regions.

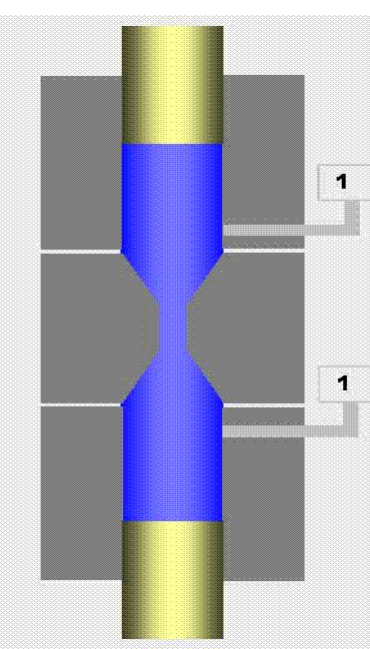


A Thermoplastic is a material that is plastic or deformable, melts to a liquid when heated and freezes to a brittle, glassy state when cooled sufficiently. It can be remelted and remoulded. Both PE and PP are semicrystalline thermoplastic polymers.

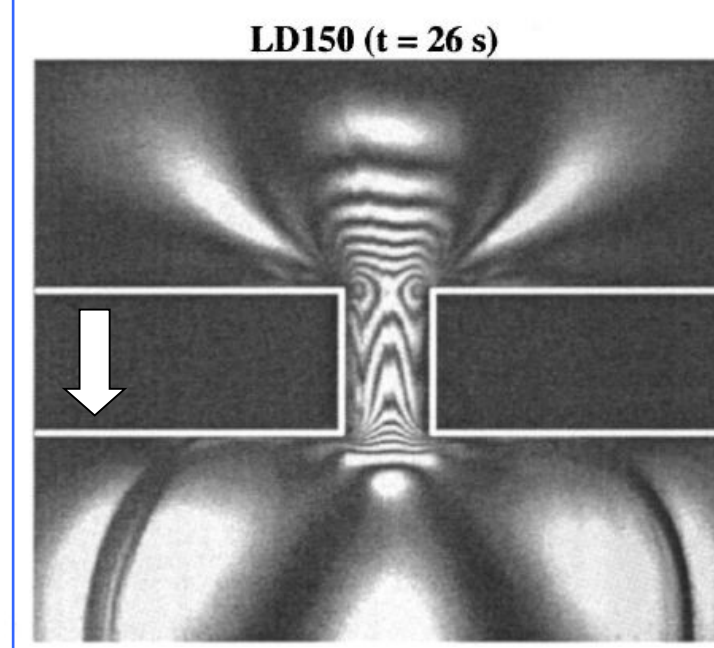


Injection moulding is a manufacturing technique for making parts from thermoplastic material in production. Molten plastic is injected at high pressure into a mold.

Multi-pass Rheometer (MPR): Dual piston, hydraulically driven capillary rheometer developed at Cambridge. The sample is driven back and forth through a narrow midsection of controlled shape. The structure development in the flowing material is followed optically or by X-ray diffraction using specially designed test-sections.



Flow birefringence (FIB) is the difference, Δn , in the indices of refraction in the flow direction and in the perpendicular direction. It is an established way to measure the stress levels in a flowing polymer: according to a stress-optical law, each fringe corresponds to an increment in the principal stress difference.



Super-cooling: Cooling a material below the temperature of an equilibrium phase change fast enough to not allow the occurrence of the transformation.

Nucleation is the onset of a phase transition in a small region.

Crystal growth: The stage following nucleation, during which the phase transition spreads outwards from the nucleating sites.

Apparent shear rate: shear rate that a Newtonian fluid would experience by flowing through the same geometry and at the same flow rate as the material studied.

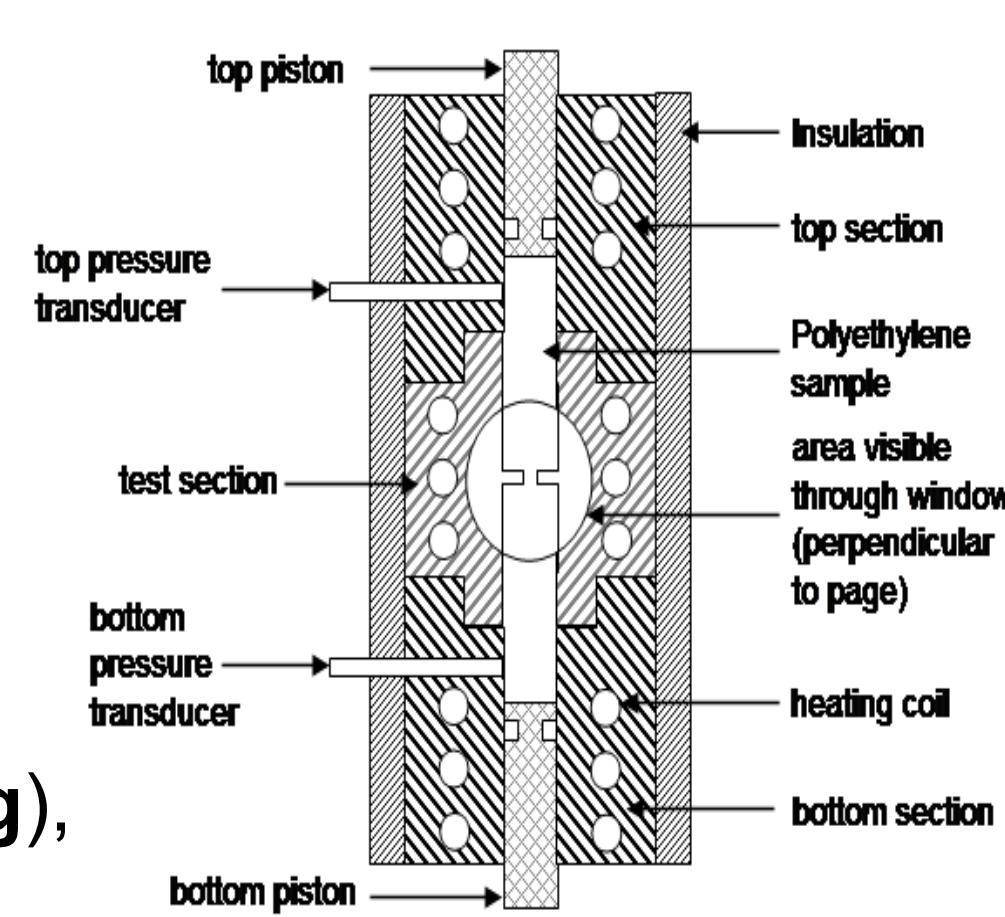
Method

Isothermal experiments were carried out in a Multipass Rheometer (MPR) on PE and PP. The polymer melt was cooled to the desired temperature and then crystallisation was induced by moving the pistons and forcing the material to flow within a narrow-section geometry. By using different mid-sections the effect of die geometry on rheological response and on FIC is investigated. The results of the MPR experiments were compared and complemented with other techniques (optical microscopy using a parallel plate shearing device, DSC, conventional controlled strain rheometry).

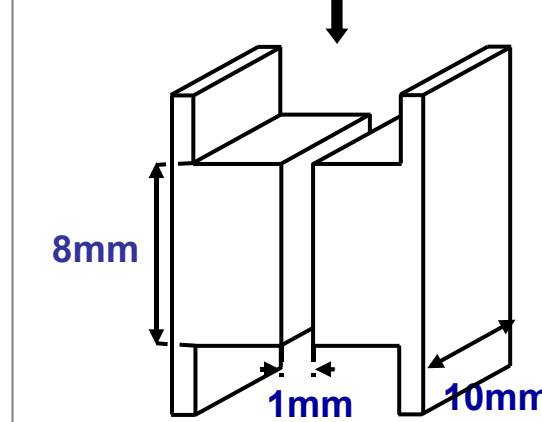
MPR with optical cell

(quartz windows & digital camera)

- Observations with crossed polars (**Stress Field**)
- Observations in bright field (**Localised FIC**)
- **Interchangeable midsections**
- Experiments at different T (**degree of super-cooling**), piston speed (**shear rate**), pass amplitude (**strain**).

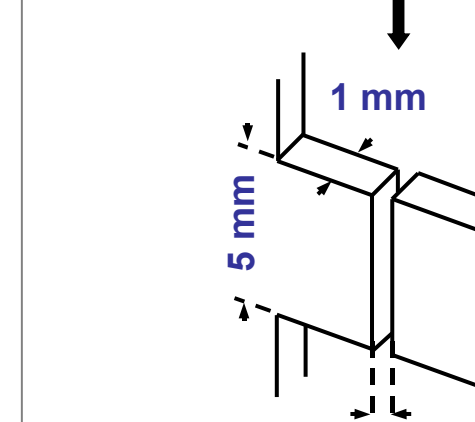


"Deep" slit



2D-flow approximation possible

"Shallow" slit



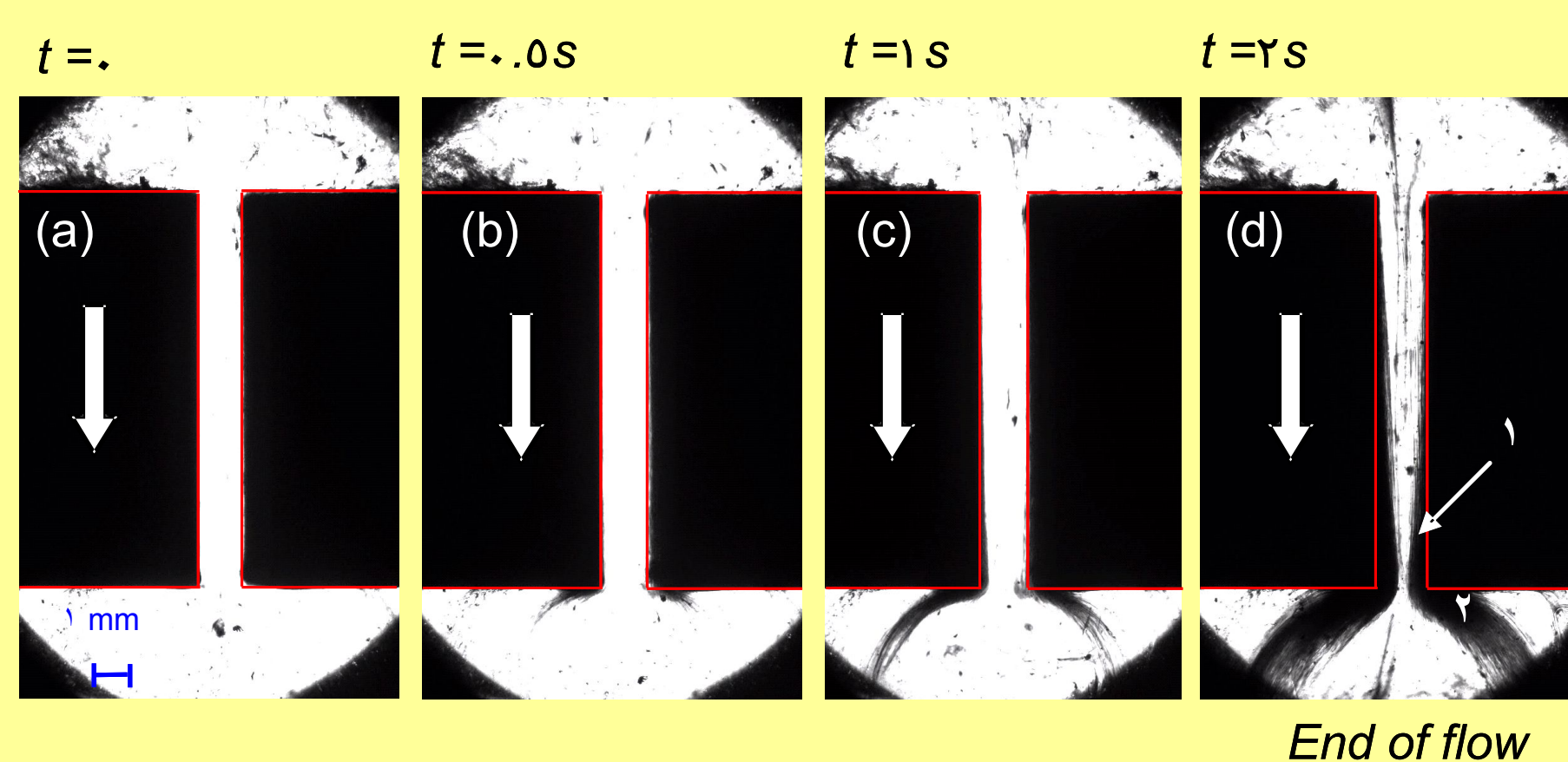
Good visualization of the morphology of the flowing polymer

Example 1: HDPE (DOW 96003E)

($\bar{M}_w = 180 \text{ kg}\cdot\text{mol}^{-1}$; $\bar{M}_n = 23 \text{ kg}\cdot\text{mol}^{-1}$; $T_m \approx 135^\circ\text{C}$)

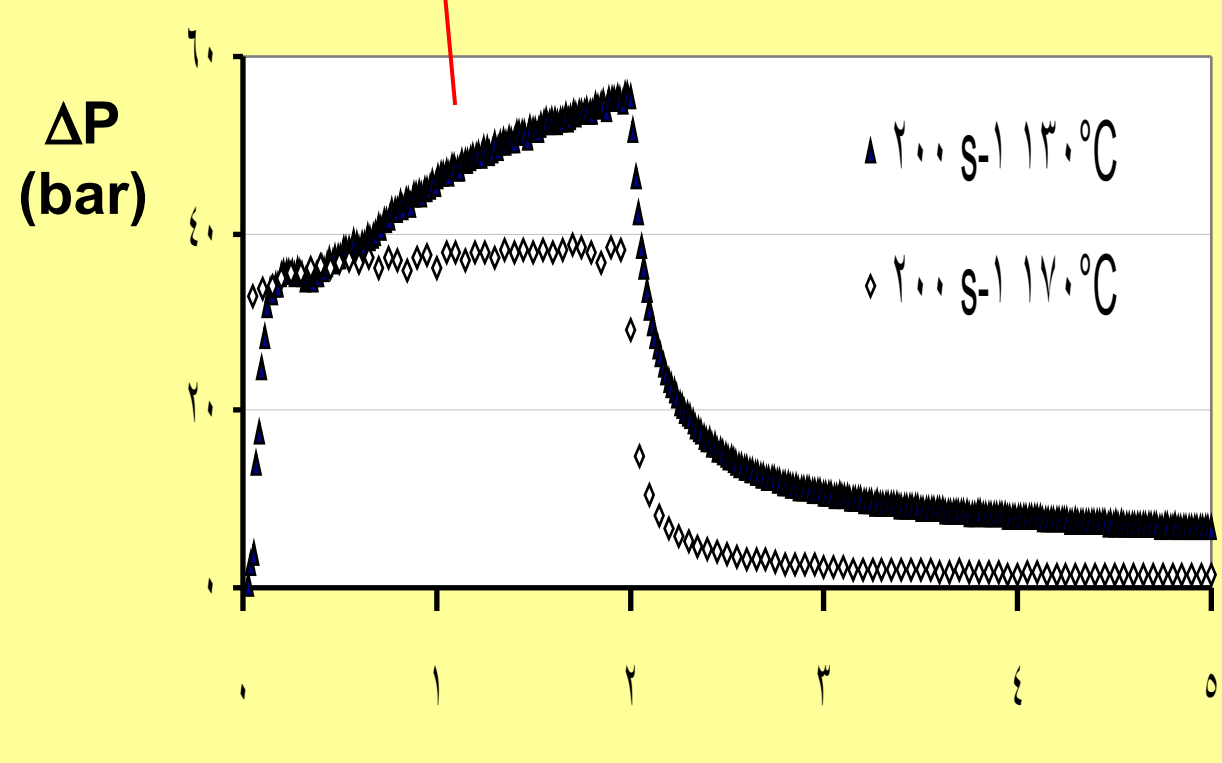
Low super-cooling

Deep slit ; $T = 130^\circ\text{C}$; $\dot{\gamma}_{w,app} \approx 200 \text{ s}^{-1}$

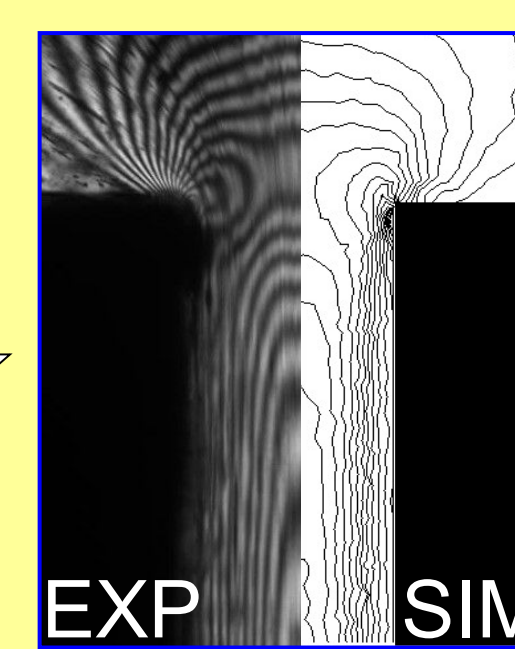


Fibrous crystallisation occurs **during flow**, originating at the walls of the slit (1) and propagating downstream (2). No further crystallisation occurs after the flow.

ΔP build up during the pass due to slit-blockage by the crystals

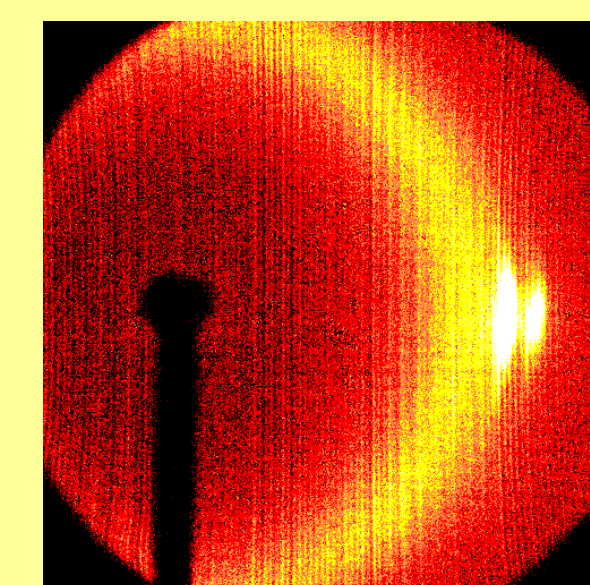


Melt flow at 140°C (just above crystallisation)
Stress field at the slit entry:
FIB vs Simulations



WAXS:

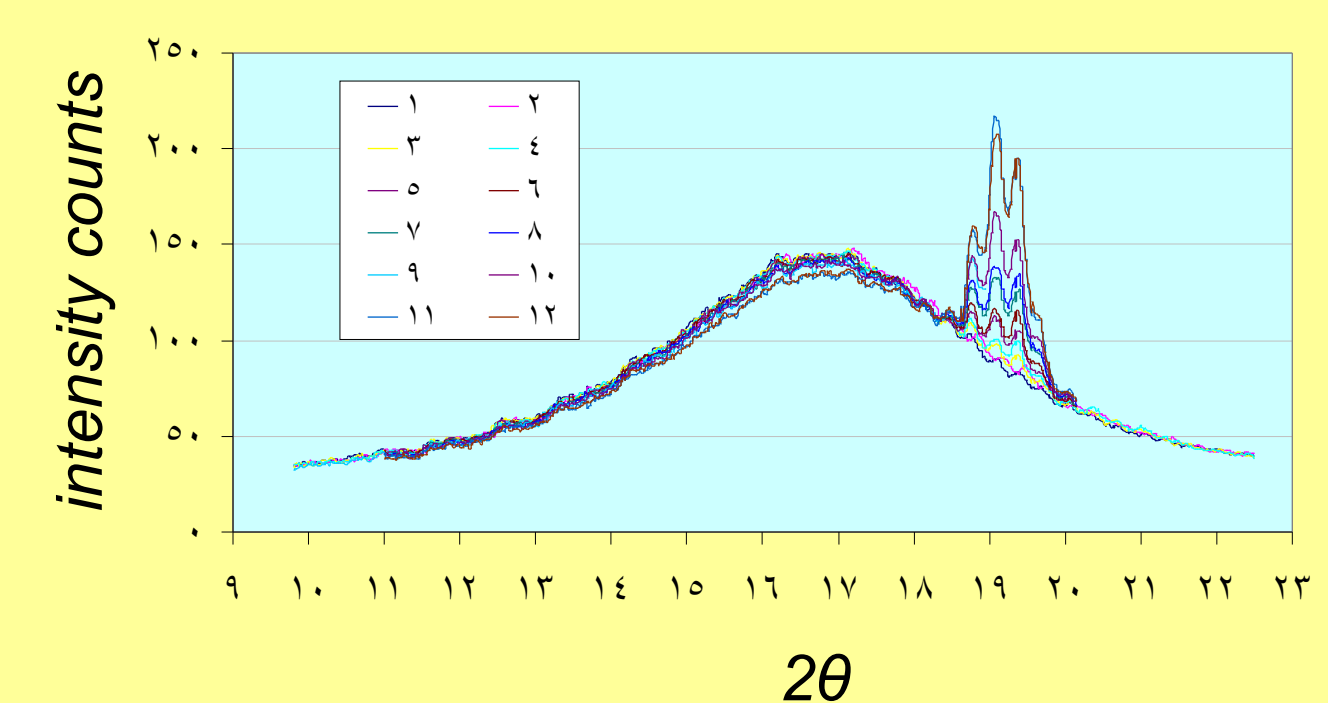
(MPR + Be capillary midsection)



- Equatorial spots \rightarrow Grow **only** during each pass (all crystals **oriented** in the flow direction)
- No spherulitic rings

HDPE; $T = 130^\circ\text{C}$

series of passes: $\dot{\gamma}_{w,app} \approx 30 \text{ s}^{-1}$

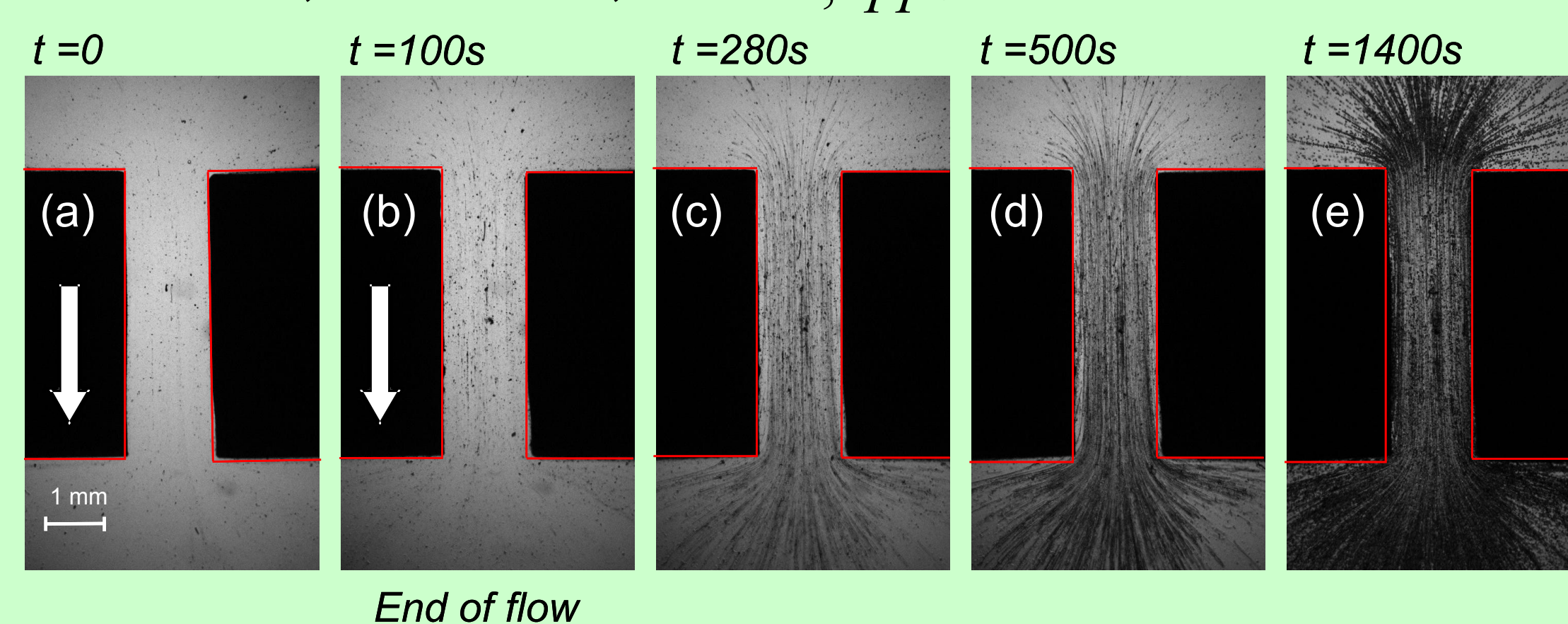


Example 2: PP (Atofina 3250MR1)

($\bar{M}_w = 213 \text{ kg}\cdot\text{mol}^{-1}$; $\bar{M}_n = 42.5 \text{ kg}\cdot\text{mol}^{-1}$)

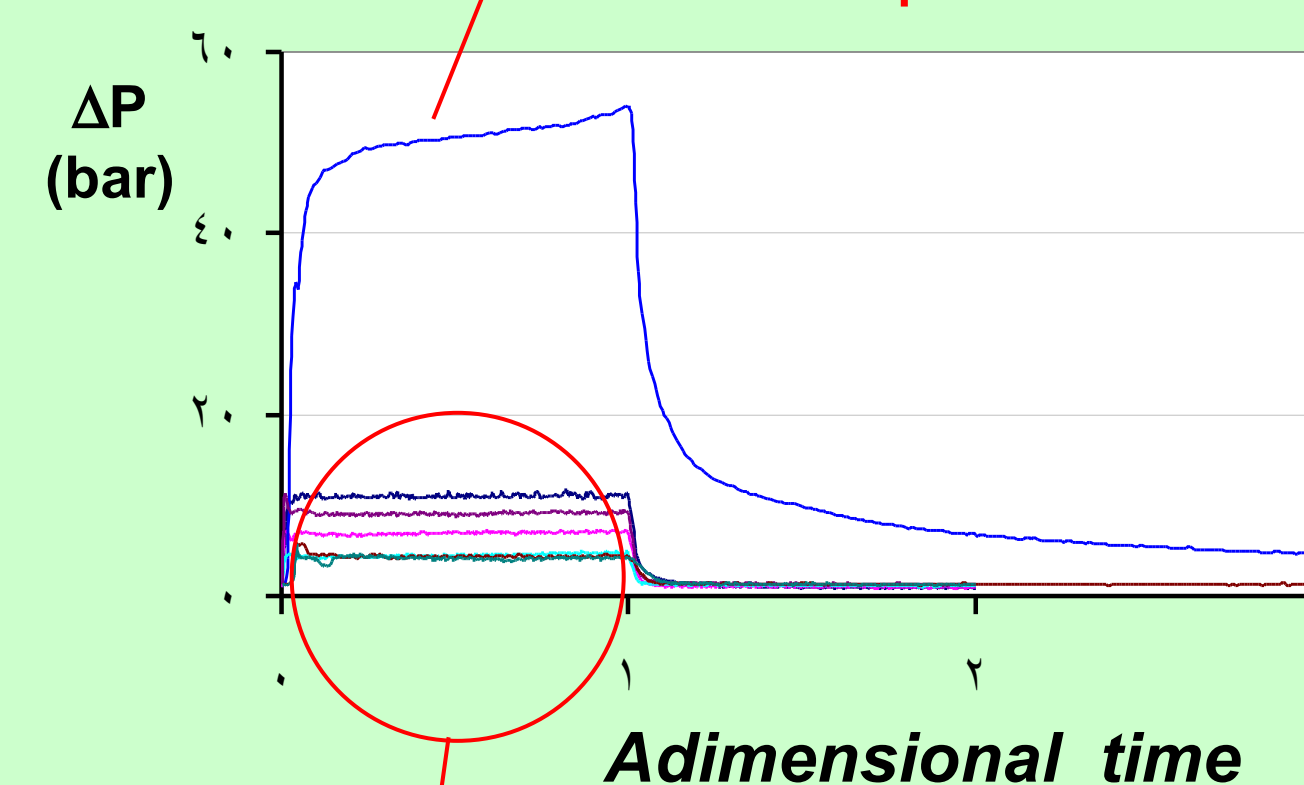
High super-cooling

Thin slit ; $T = 134^\circ\text{C}$; $\dot{\gamma}_{w,app} \approx 100 \text{ s}^{-1}$



The line-nuclei that dictate the crystal morphology are generated during flow, but most of the crystallisation process occurs in the form of lamellar and spherulitic growth **after the flow** has stopped

High $\dot{\gamma}$ (4000 s^{-1}):
 ΔP build up



Low $\dot{\gamma}$ ($20 - 100 \text{ s}^{-1}$):
NO ΔP build up during flow

Conclusions & future work

The basis has been laid for a full experimental characterisation of the FIC behaviour of PE and PP in relation to the main processing parameters.

Qualitative diagrams showing the crystal morphology in isothermal FIC MPR experiments as a function of temperature and wall stress were created for both polymers and represent the starting platform on which the modelling work will develop.

The stress (τ), orientation (Φ) and stretch (λ) of the high molecular fraction of the polymer chains at local positions in the flowing polymer will be identified and related to the nucleation and growth parameters of an Avrami-type crystallisation model.

In order to obtain more quantitative information, experiments on polymers of well known architecture will be carried out.

References:

- Saquet, O. *et al.* (*J. Mat. Sc.* 35 (2000), 5247-5253)
- Lee, K. *et al.* (*J. of Rheology* 45(6) (2001), 1261-1277)
- Mackley, M.R. *et al.* (1995) (*J. of Rheology* 39 (6) (1995), 1293-1309)

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