Family matters

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Family Matters

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Introduction

The microstructure of semi-crystalline polymer products can be fascinating and extremely complex. For example, chains that have been extended by flow can act as nucleation sites for lamellae that grow radially outward. This morphology was aptly named shish-kebab (Fig 1).

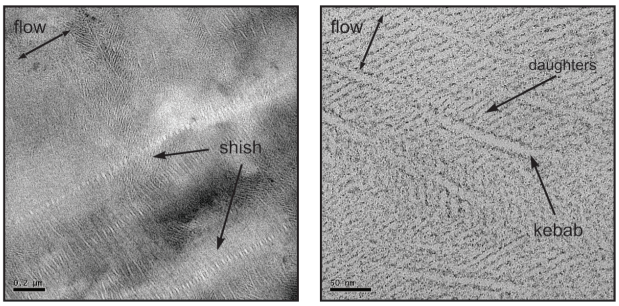

Figure 1: TEM picture of shish-kebab morphology[1]

On the imperfections in the kebabs, so-called daughter lamellae nucleate (Fig 2). The aim of this work is to investigate the crystallization kinetics of both parent (kebabs) and daughter lamellae.

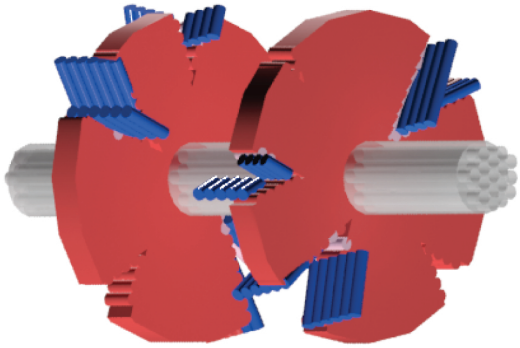

Figure 2: Schematic representation of shish-kebab structure with parents (red) and daughters (blue).

Experiments

Slit flow experiments combined with in-situ synchrotron x-ray experiments were performed at the ESRF, Grenoble.[2] Recently, a detector with an unprecedented sample rate of 30 Hz became available, allowing us to probe structure formation for extremely strong flows.

Simulations

A novel crystallization model was developed that considers parents as cylindrical domains growing radially outward and daughters nucleating homogeneously in this volume. Furthermore, crystal growth rate was taken time-dependent due to both deformation during flow and heat release during crystallization.

Results

Simulations and experimental results are compared in Fig 3. The area under 110 reflection peak is shown, which directly correlates to crystalline volume fraction.

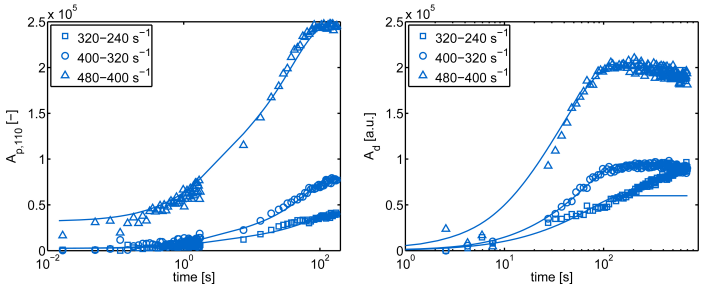

Figure 3: Area of 110 reflections in WAXD signal for parents (left) and daughters (right). Symbols show measurements, lines show simulations.

Conclusions

Simulations and experiments show excellent agreement, validating key assumptions in our modeling:

- Nucleation rate of daughter lamellae is proportional to the radius of parent crystals, indicating a nucleating mechanism as shown in Fig 2.
- Crystal growth rate of kebabs is increased during flow, which in strong flows is of paramount importance for the final crystal structure.
- Locally, temperature can increase by as much as 6 °C in a matter of seconds due to heat of crystallization.

References

[1] T. van Erp. Ph.D. thesis, Eindhoven University of Technology (2012).

[2] Z.Ma, et al. *Macromolecules* **45** (2012), 4216–4224.