Effect of flow and pressure on structure formation of LLDPE

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Introduction

Influence of flow on crystallization of polymers has been extensively studied: it is able to enhance kinetics and promote peculiar morphologies like shish-kebab (Fig 1). The effect of pressure is often neglected: in this work we demonstrate that pressure has a huge influence on crystallization behavior of linear low density polyethylene (LLDPE).

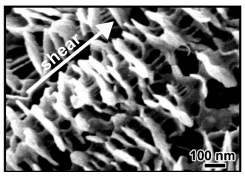

Figure 1: *Shish-Kebab structures: fibrillar nuclei inducing the growth of oriented crystals.*

Approach

Methods:

- combining slit flow and in-situ SAXS/WAXD (Fig 2) on LLDPE.
- 4 different flow conditions/piston speeds at 117°C for 1.5 s.

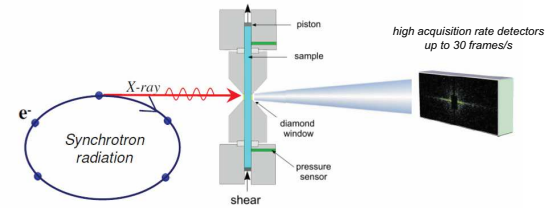

Figure 2: *Combined in-situ X-ray scattering and slit flow rheometry.*

Outcome:

- Rheology - deviation from regular viscoelastic response.
- WAXD - crystallinity evolution from A_{110} (area underneath 110 peak).
- SAXS - informations about morphology from equatorial (shish) and meridional (kebab) intensities.

Results and Discussion

The pressure responses show an upturn during flow due to structure formation which is evident from the evolution of WAXD intensity (Fig 3). Surprisingly, crystallinity decreases immediately after the cessation of the shear pulse, indicating melting of part of the structures produced during flow .

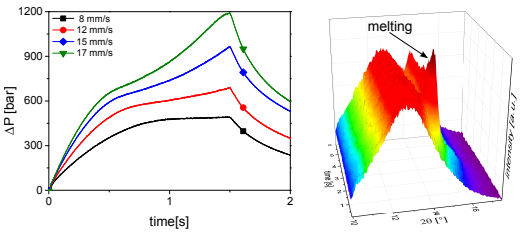

Figure 3: *Left: Pressure drop between the pressure transducers for all flow conditions. Right: Time evolution of WAXD intensity for the fastest piston speed.*

Equatorial intensities, related to scattering of shish, grow during flow and keep increasing until they reach a plateau value whereas meridional intensities, correlated to kebabs, show an increase and a subsequent diminution. Meridional intensities and A_{110} superpose almost perfectly in the time interval when relaxation is observed. Unambiguously, the decrease in crystallinity is related to melting of kebabs (Fig 4).

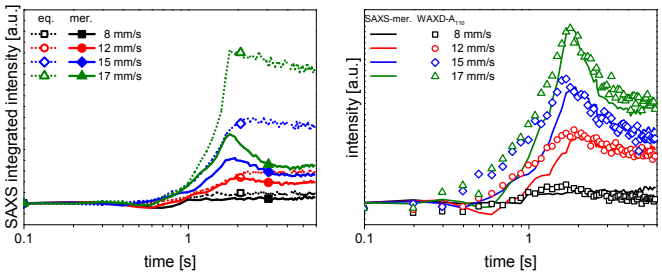

Figure 4: *Left: Time evolution of SAXS integrated equatorial and meridional intensities. Right: Comparison between SAXS meridional intensities and area underneath (110) reflection.*

Pressure shifts the equilibrium melting temperature and consequently the undercooling according to Clausius-Clapeyron relation [1]. It can promote the crystallization of metastable thinner lamellae on growing kebabs which melt when pressure/undercooling decrease compromising their thermodynamic stability. Use of a structural model developed by B. Hsiao [2] to fit SAXS data permitted us to calculate average dimensions of kebabs and propose the model shown in Fig 5.

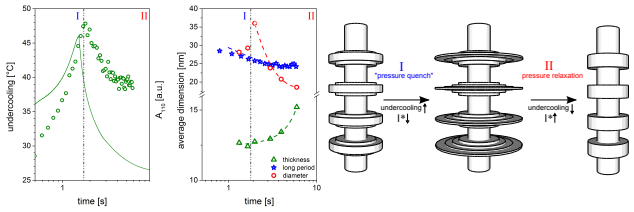

Figure 5: *Left: Time evolution of A_{110} and undercooling evaluated according to Clausius-Clapeyron equation for the fastest piston speed. Middle: Average dimensione of kebabs. Right: Proposed model for "pressure quench" and "pressure melting" during and after flow.*

Conclusions

In processing-like conditions, pressure plays a key role in flow induced crystallization of polymers with a low tendency to crystallize like LLDPEs. It can influence structure formation by promoting nucleation of metastable crystals at temperatures above the nominal melting point.

References

1. Wunderlich, B. *Macromolecular Physics; Academic Press*, **1980**; Vol. 3.
2. Avila-Orta, C. et al. *Polymer*, **2005**; 46 (20), 8859-8871.

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