ESRF	**Experiment title:** Crystallization in polyolefins using commercial polymer extrusion instrumentation.	**Experiment number**: ME-967
Beamline: Bm26b	**Date of experiment**: from: 14/02/05 to: 18/02/05	**Date of report**: 18/08/05
Shifts: 12	**Local contact(s)**: F. Meneau	*Received at ESRF:*

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Experimental:

The processing of semi-crystalline thermoplastics relies on the shaping of molten materials in either moulds or dies. The stabilization of the product shape is produced by the crystallization process. During crystallization a microstructure develops which controls the mechanical and aesthetic properties of the final polymer material. Here, results are given when real time processing of polyethylene from a commercial extruding instrument[1-3] has been performed. The instrument has been installed on the Dubble CRG beamline BM26b, where Small Angel X-ray Scattering (SAXS) patterns have been obtained from the polyethylene tape, whilst the extruder has been running. Figure 1, shows the extruder set-up on the beamline and the positions of the X-ray detector. The haul-off motor has been replaced with a Rheotens system which allows constant force haul-off to be achieved on the extruded tape. This avoids complications that were previously incurred when the tape was merely wound up on a spindle which changed the haul-off velocity as the tape volume increased, giving a non-constant elongation in the tape.

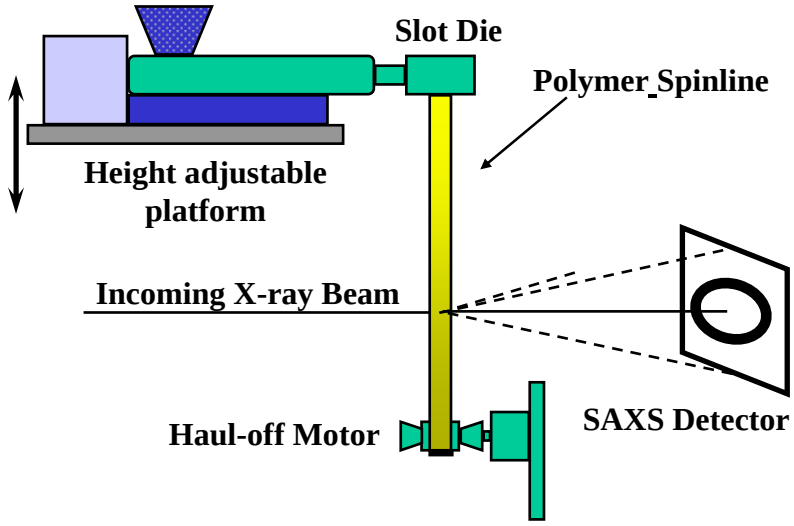

Figure 1. The extruder set-up on Dubble.

Results and discussion:

The SAXS data was taken at the a steady state point on the tape. Here, the screw speed was constant at 3Hz, the extruder height varied in between data sets and the haul-off monitored at a constant force. The data were taken at several heights and haul-off speeds (in rpm) at a constant extruder height. In Figure 2, SAXS data are given representing an increasing haul-off speed, when the extruder die head is at a height of 760 mm above the incident X-ray beam. From the SAXS patterns it is clear that the increase in haul-off speed increases the orientation in the tape, given by the lobes pictured in the meridional direction on each pattern. This also indicates the development of a fibril/lamellae type structure in the tape. At low haul-off speeds e.g. 60 rpm, the SAXS pattern indicates a greater isotropic lamellae structure, this is due to the relaxation of the chains. As the haul-off speed is increased, the chains become more elongated, however there is also in increase in temperature at this point

on the tape, being due to the tape having less time to cool as it is effectively pulled off at a faster rate. The increased structure though, is seen due to the increase in elongated molecular chains providing more nucleation sites for the fibrils to grow. Clearly this is seen as the haul-off speed increases to 300 rpm. In Figure 3, similar SAXS patterns are shown but here the extruder height has been increased to 1000 mm. The screw speed is constant still at 3Hz, there for effectively the same amount of material is travelling over a greater distance at similar haul-off rates, hence the tape becomes more narrow. This will effectively increase the molecular elongation and temperature at the point when the X-ray beam hits the tape. In the SAXS patterns similar orientation is seen to develop in the macromolecular structure as the haul-off speed is increased. The increased height gives greater levels of molecular elongation and therefore more nucleation sites for the fibril structuregrowth to occur. Even at the low haul-off speeds much initial orientation is seen in the SAXS patterns rather than isotropic scattering, indicating that the molecules have not relaxed in this instance. Finally, further evidence from the SAXS patterns of the high molecular elongation is indicated by the appearance (at high haul-off speeds) of equatoial scattering streaks. This shows that a high density of molecular chains are oriented in the length of the tape. The lobes on the meridian indicate the fibrils/lamellae which grow perpendicular to these elongated molecular chains at the sites of nucleation. On increasing the extruder height even further, the oriented structure development and chain elongation is again more prominent in the SAXS patterns, along with the appearance of the equatorial streaks form the highly elongated chains.

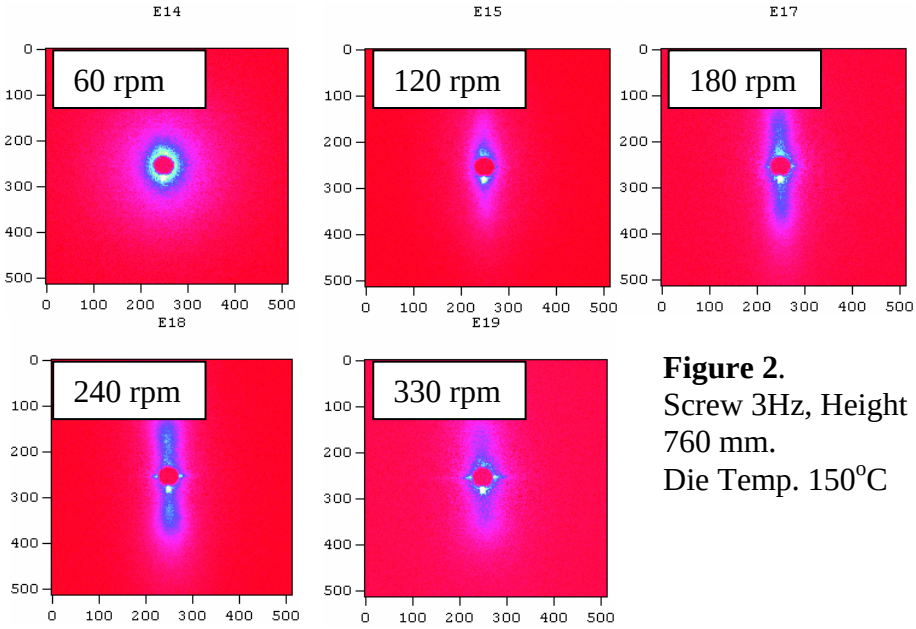

Figure 2.
Screw 3Hz, Height 760 mm.
Die Temp. 150°C

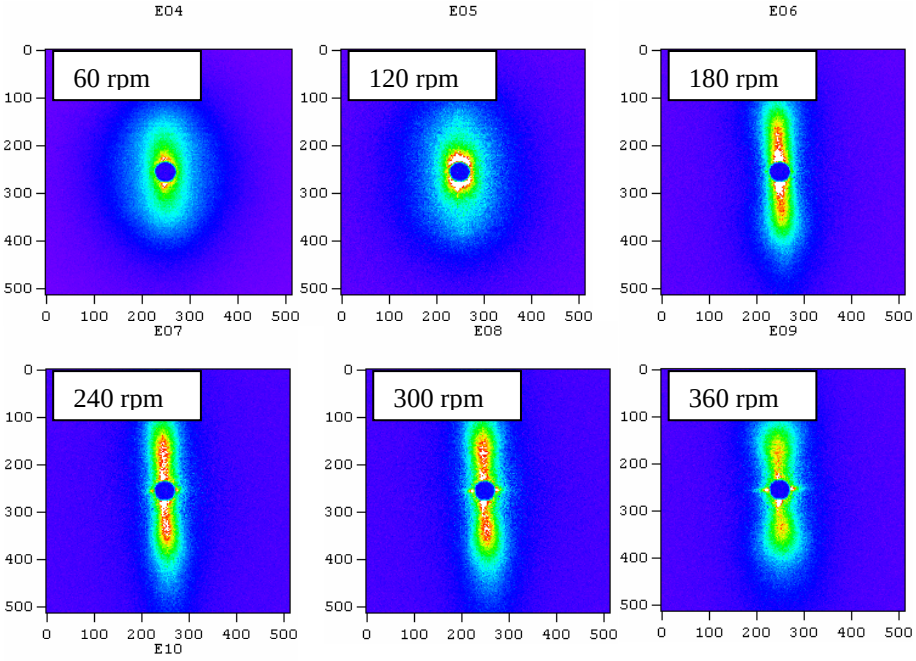

Figure 3. Screw 3Hz. Height 1000 mm. Die Temp 150°C.

1) N.J. Terrill, J.P.A. Fairclough, B.U. Komanschek, R.J. Young, E Towns-Andrews and A.J. Ryan, *Polymer* 1998, **39,** 2381

2) M. Cakmak, A. Teitge, H. G. Zachmann and J. L. White, *J. Poly. Sci.* Part B, 1993, 31, 371.

3) E.L. Heeley; T. Gough; W. Bras; A.J. Gleeson; P.D. Coates & A.J. Ryan. Nuclear Instruments and Methods in Physics Research Section B: Beam Interaction with Materials and Atoms, In press 2005.