



	Experiment title: A shear induced crystallisation study of poly(ethylene terephthalate) with enhanced properties	Experiment number: SC-1480
Beamline: Bm26b	Date of experiment: from: 14/5/04 to: 17/5/04	Date of report:
Shifts: 9	Local contact(s): W. Bras	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): E. Heeley* and C. Hurley* (University of Sheffield, UK) D. Sutton*, T. Hanley*, R. Knott* (ANSTO, Australia) R. Burford* (University of New South Wales, Australia)		

Report:

A series of PET samples were produced with varying degrees of branching via a reactive extrusion process. The main objective for this process is to increase the melt strength of our standard "virgin" PET grade so that a wider range of processing options are available, e.g. extrusion blow moulding. A control sample (070999A) was run through the extruder but without any of the branching additives present. As the molecular weight of PET is reduced by processing, the control sample will have the lowest intrinsic viscosity (IV) of all the samples. For the SAXS experiments, the samples were heated in a Linkam shear cell at 300 °C for 5 minutes to remove any thermal history, then quenched at 30 °C per minute to 280 °C. SAXS Data collection was started and once one melt frame had been collected, a shear of 53 s⁻¹ was applied for 2 seconds. On cessation of the shear, the temperature was again quenched at 30 °C per minute to 245 °C & held at this temperature to observe the crystallisation process. Figure 1 shows a series of time lapsed SAXS images for each of the samples.

In general, figure 1, shows that as the degree of branching is increased, the crystallisation kinetics increase, as is the degree of anisotropy. By increasing the degree of branching, the relaxation time after shear of the high molecular weight chains is increased due to a greater number of entanglements. This means that the high molecular weight chains remain oriented longer after shear and may act as nucleating sites for the lower molecular weight chains to crystallise. This extra nucleation increases the overall kinetics and results in the crystalline lamellae being oriented perpendicular to the shear direction. The structure becomes fixed by crystallisation resulting in the anisotropic SAXS images for the highly branched materials. For the low IV materials, the lack of high molecular weight chains means that the polymer chains are able to relax fairly quickly after removal of shear. Therefore no anisotropy is observed in the SAXS images & crystallisation proceeds more slowly. In this case, the material with lower molecular weight chains are able to move more freely and crystallise slightly faster.

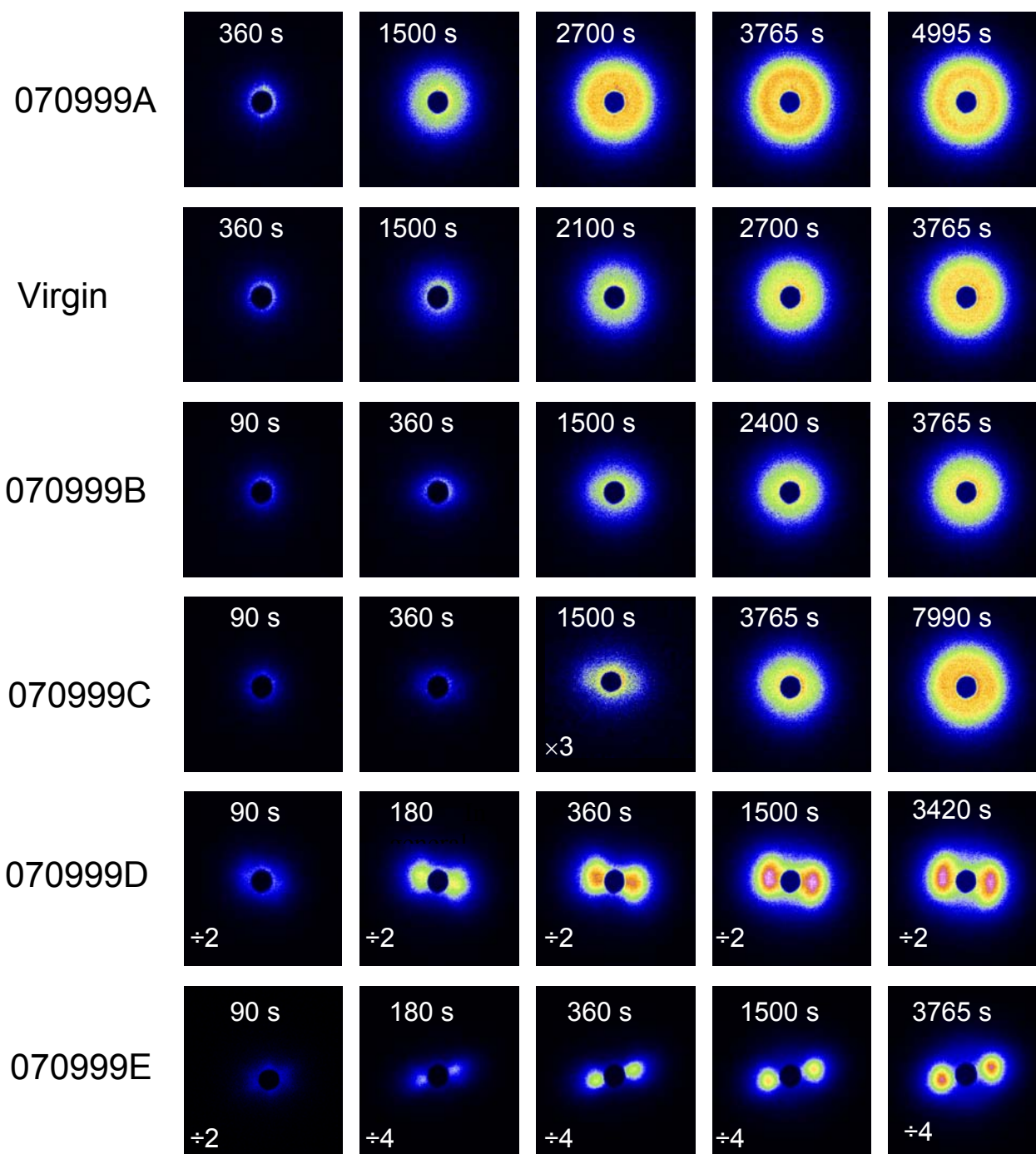


Figure 1 SAXS data for Poly(ethylene terephthalate) (PET) samples having undergone shear. The elapsed time in seconds, since the application of shear is shown on each image. All images are displayed on the same intensity scale, those images that required scaling have the scale factor displayed on the image. The degree of branching and IV increases down the list.

Conclusions

- High molecular weight chains play a key role in shear-induced crystallisation
 - due to increased entanglements
 - which result in slower relaxation times after shear
 - which leads to enhanced 'nucleation' effects
- Faster crystallisation kinetics leads to oriented structures and therefore oriented SAXS images
- Branching agents have clearly altered the properties of these high melt strength PETs (HMS-PET).