<b>ESRF</b>	<b>Experiment title:</b> Time-resolved SAXS/WAXS studies of strain-hardening and structural changes in branched poly(ethylene terephthalate) (PET) under industrial processing conditions.	<b>Experiment</b> <b>number</b> : SC-1945
Beamline:	Date of experiment:	Date of report:
ID02	from: 25/2/06 to: 28/2/06	18/02/07
Shifts:	Local contact(s):	Received at ESRF:
9	Dr. T. Narayanan	
Names and affiliations of applicants (* indicates experimentalists):		
A Mahendrasingam*, DJ Blundell*, M Parton* and W Fuller		
School of Chemistry and Physics, Keele University, Staffs, ST5 5BG, UK		
A I Dairanieh		

BP America Inc, Mail Code E-1D(301-1127), 150 Warrenville Road Naperville, IL 60563-84460, USA

## **Report:**

In this study we have recorded simultaneously SAXS/WAXS/Strain developed/Force applied during uniaxial deformation of linear polyethylene terepthalate (L-PET) and branched polyethylene terepthalate (B-PET) using the Keele drawing camera. In this report we describe the results obtained during uniaxial deformation of PET at temperatures 86 °C, 96 °C, 116 °C and 126 °C at draw rates from 1125% min<sup>-1</sup> to 72000% min<sup>-1</sup>.

Although both polymers showed similar overall trends in behaviour with changes in draw rate and draw temperature, there were distinct differences in mechanical response and crystallisation, particularly in relation to draw temperature.

Examples of WAXS patterns showing the differences in behaviour between the higher and lower temperatures are illustrated in Figures 1 for 96°C at draw rate of 12sec<sup>-1</sup> and in Figure 2 for 116°C at 0.375sec<sup>-1</sup>. Figure 1 shows that for both polymers there is a progression from an

isotropic amorphous halo to diffuse equatorial spots at 0.2sec (close to the end of deformation) followed by the appearance of sharp diffraction spots of the highly oriented



crystal phase. At the higher temperature in figure 2 the deformation produces a slight equatorial intensification of the diffuse halo. The crystalline reflections indicate a greater spread of orientation

than at the lower temperature. They are more difficult to resolve, particularly for the B-PET in the early stages of crystallisation. In the L-PET there is a split in some of the reflections indicating a tilt in the crystals with respect to the draw direction. The onset of oriented crystallisation starts at the end of the mechanical extension within the neck. The crystallinity

increases rapidly and then asymptotes to a final level. This crystallisation behaviour is well documented in our previous investigations of L-PET, where the delay in the onset of the



crystallisation until the end of the deformation was attributed to the draw rate being faster or comparable to the chain retraction process within the entangled network. With an increase in temperature to 116°C the differences between the polymers becomes more marked. The B-PET shows a more gradual yield process with a more uniform draw-down along the length of the specimen whereas the L-PET continues to show a more prominent neck. The onset of crystallisation in both polymers occurs before the end of the extension so that significant crystallisation is occurring during extension. However in the L-PET the onset of crystallisation occurs around a draw ratio of 2.5 and is closer to where the draw ratio in the neck has stabilised. The onset in the B-PET occurs at lower draw ratios of around 1.5.