ESRF	**Experiment title:** In-situ X-ray diffraction of the crystallization of poly(hydroxy butyrate) during extension	**Experiment number**: ME8
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Introduction

The ageing of poly(hydroxy butyrate), (PHB) and its copolymers is well established. Over a period of some weeks after preparation, PHB samples suffer a pronounced change in mechanical properties. The extension to break falls from an initial value in the region of 100% to about 2%. At the same time the modulus increases. These generally detrimental changes have been a major contributing factor to the lack of progress in the widespread use of PHB in many applications.

Recent work in Bristol and Moscow has thrown new light on the ageing process of (PHB). We have prepared fibres of PHB over a much wider range of processing conditions than had previously been possible. Both directly from the melt - the work from Russia, and from glassy polymer- the work from Bristol.

We have both found that the oriented fibres do not show any detrimental ageing, at least in the first few months.

In the experiment we performed simultaneous stretching and X-ray experiments to determine why some oriented samples do not display the ageing behaviour while others do so.

We are in the process of preparing a publication on the work performed at ESRF.

Experimental method

We used a Hounsfield testing machine (from Bristol) to stretch samples of PHB which had been quenched to a glass and then heated to a temperature in the range 5°C to 10 °C (i.e. just above the glass transition temperature) in the X-ray beam. Samples were stretched at a range of rates up to 50cm per minute. We recorded the wide (and some of the low) angle scattering and its changes during stretching.

Results

We collected a full 2-D diffraction pattern every 3 seconds. At low drawing speeds (up to and including 25cm per minute) the PHB crystallizes at all extensions in the normal form. At 50 cm minute a different behaviour is seen. Almost as soon as the stretching begins a new reflection appears which cannot be indexed using the normal PHB cell (see figure 1a). This reflection is oriented along the equator and reaches its maximum intensity within 10 seconds, a second reflection appears on the first layer line at the same time. Later, on warming to room temperature, the normal PHB crystals appear in a highly oriented form but the additional reflections remain (see figure 1b). From the low angle scattering it is clear that the lamellae are oriented normal to the stretching direction.

If the sample is relaxed before the normal crystals form then the new reflection disappears.

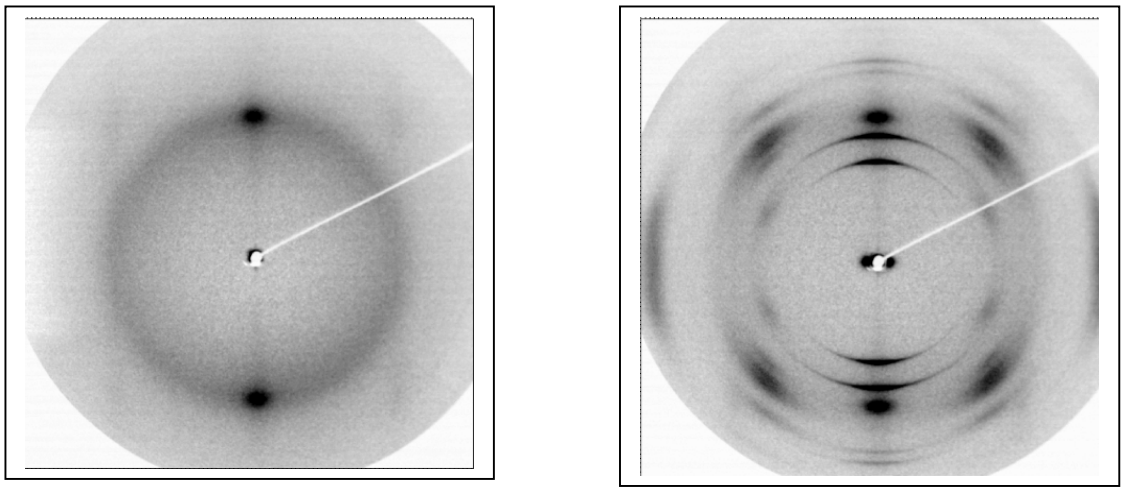

Figure 1: On the left in figure 1a the two intense reflections are the new reflections that do not index on the normal PHB lattice. In figure 1b on the right these same reflections can still be seen superimposed on the normal pattern of a sample after it had been warmed to room temperature. Note the stretching direction is horizontal

Discussion

We believe that the new reflection arises from the crystallization of a stretched "rubber" made up of entangled amorphous PHB chains. In such a case it is unlikely that the chains would be able to have the anti-parallel packing that occurs in the normal crystals leading to a different diffraction pattern. These "stretched rubber" crystals would be stabilised by the applied external extension (and melt when the extension is removed). When the remaining polymer crystallizes around these new less ordered crystals they can be stabilised by the resulting constraints.

We are in process of performing further experiments to determine the actual crystal structure of the new form and to correlate it with the removal of the ageing processes.