SYNCHROTRON STUDIES OF POLYMERS AT HIGH SPATIAL AND TEMPORAL RESOLUTION

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ABSTRACT

Developments in X-ray synchrotron radiation sources and electronic area detectors have allowed the development of new X-ray diffraction techniques to investigate polymeric materials at high temporal and spatial resolution. These developments are illustrated by studies of poly(ethylene terephthalate) (PET). The fabrication of films and containers of PET typically involves mechanical deformation at elevated temperatures close to its $T_g$. Such processing can have major effects on the degree of polymer orientation and crystallinity and hence on the physical properties of the material. This paper describes the time-resolved X-ray diffraction technique developed to investigate the strain-induced crystallisation in PET under industrial processing conditions with 40 milliseconds time resolution. The investigation of the structural variation in orientation and crystallinity across the wall of a container fabricated from PET using an X-ray beam as small as 2 $\mu$m diameter is also described. The potential for more general application of these techniques in the study of other polymer materials is indicated.

INTRODUCTION

X-ray diffraction provides one of the most powerful techniques for characterizing polymer orientation and crystallinity and hence for exploring the relationship between industrial processing conditions and the properties of the finished polymer products. The increasing availability of synchrotron radiation sources during the last decade with a brilliance in the X-ray region many orders of magnitude greater than conventional laboratory sources has dramatically extended the power of diffraction techniques for investigating polymer conformation and organization and in particular the variation of these characteristics with a time-resolution of 40 msecs. i.e. on time-scales comparable to those of industrial processing. An important aspect of this has been the availability of electronic area detectors, which allow diffraction patterns to be displayed in real time. The information obtainable from these techniques is of fundamental importance in understanding the strain-induced crystallization process, which occurs when polymers such as PET are oriented close to their $T_g$.

The development of the microfocus beamline ID13 at the ESRF, the availability of CCD based data acquisition systems and a high-precision computer-controlled X/Z stage allows diffraction data to be recorded with an X-ray beam diameter as small as 2 $\mu$m in a reasonable time scale and has enabled the investigation of the structural variation in polymeric materials with high spatial resolution.
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This paper will discuss the experimental and analytical techniques developed for recording and analysing temporally and spatially resolved X-ray diffraction data with examples from PET. However, these techniques are generic and applicable in the study of a wide variety polymeric materials.

EXPERIMENTAL

Instrumentation

Instrumentation for time-resolved studies consists of: (i) drawing cameras which can deform polymer samples uniaxially\(^1\) and biaxially\(^2\) at up to 72000\% min\(^{-1}\) at temperatures up to 350°C, (ii) a detector system with three synchronised CCD cameras which allows simultaneous recording of wide angle X-ray scattering (WAXS), small angle X-ray scattering (SAXS) and strain data\(^3\). Strain rate and draw ratio at the point in the specimen from which the diffraction data is recorded is calculated from changes in the position of reference lines on the specimen and also by integrating the diffracted intensity from the WAXS pattern. The power of the instrumentation is illustrated by recent studies of strain-induced crystallisation in poly(ethylene terephthalate) (PET) at the European Synchrotron Radiation Facility (ESRF)\(^4-9\).

Instrumentation for high spatial resolution studies consists of: (i) a computer-controlled high-precision X/Z stage with a reproducibility of 0.1\(\mu\)m, (ii) glass capillary optics to produce a beam with diameter of \(~2\mu\)m at the specimen, (iii) CCD cameras to record WAXS or SAXS data and monitor the specimen position and state.

For all applications the X-ray data was recorded using an integrating Photonic Science X-ray CCD camera and a Synoptics i860 framegrabber. This detector system is capable of displaying the data in real-time while the data is being recorded. The enormous advantage of being able to perform temporally and spatially resolved experiments in real time is a crucial factor in deciding to use CCD detectors rather than for example image plates. The data from the detector system is digitised at the video rate (25 frames sec\(^{-1}\)) using a Synoptics i860 framegrabber with 128Mb on board memory in color or mono mode. This feature enables the framegrabber to be operated in color mode with three synchronised mono video signals from WAXS, SAXS and the sample image. The framegrabber is hosted in three ISA slots of a 100 Mhz Pentium PC and operated by theXNIX operating system, which is a variant of UNIX. Digitised data is downloaded from framgrabber memory to SCSI disk and archived to DAT tapes.

Analytical techniques

A typical series of diffraction patterns and corresponding video images of the sample recorded during the mechanical deformation of PET at 90°C and 72000\% min\(^{-1}\) with 40 milliseconds time resolution is shown in figure 1. It can be seen from figure 1 that the draw is completed by frame 8 where the diffraction pattern corresponds to a well oriented amorphous pattern with a diffraction maximum at \(~0.28\ \text{Å}^{-1}\). Frame 9 shows the first detectable crystalline reflection around the amorphous diffraction at \(~0.28\ \text{Å}^{-1}\) and subsequent frames show the gradual
development of the {010} reflection. Estimates of the crystallinity were obtained by fitting a Pearson VII function to the {010} reflection of the radial scan along the equator which is shown in figure 2. In order to quantify the development of orientation during deformation but before crystallization, azimuthal circular scans were extracted from the diffraction pattern at a reciprocal space vector of ~ 0.28 Å⁻¹. This corresponds to the position of the maximum in the equatorial scans of the diffuse diffraction observed at the onset of crystallization. There is an expectation that this azimuthal profile is closely linked to the orientation distribution of the segments making up the PET chain. The azimuthal scan and the fitted curve from a typical deformation experiment are shown in figure 3. The azimuthal profiles were used to calculate the orientation order parameter \( <P_2(\cos \theta)> \), using the expression derived by Lovell and Mitchell\(^{10}\), where \( \theta \) is the angle between the segment direction and the draw direction.
Draw ratio and rate have commonly been derived from the movement of the jaws holding the sample assuming that the sample deforms uniformly. We have improved on this approach by measuring the change in the spacing of ink marks on the video images of the sample. There are still drawbacks to this method for the following reasons: (i) due to local necking the draw ratio and rate where the diffraction pattern is recorded is underestimated,
Figure 4

Figure 5
(ii) Data analysis is time consuming due to the high volume of data generated in time-resolved experiments. Therefore, we have developed a semi-automatic method to analyse the data from these experiments. This method allows draw parameters to be calculated semi-automatically for each frame with a high degree of accuracy from the integrated WAXS. The method involves prior calibration from parallel measurements of changes in ink marks on the region of the specimen where drawing is highly uniform. If we assume that the sample density remains constant during the draw, then for a draw ratio of $\lambda$, the thickness of the sample in the beam direction would be proportional to $1/\sqrt{\lambda}$. Thus the square of the inverse of the integrated intensity should be directly proportional to $\lambda$. In a typical experiment draw ratios calculated from integrated WAXS and measured from video images are shown in figure 4. In practice the deformation is not ideally uniaxial and in order to obtain absolute values for the draw ratio it is necessary to use a calibrated curve from experiments in which the corresponding video image and integrated intensity measurements were made on the same specimens. Such a calibration curve is shown in figure 5. Using this calibration curve, the calculated draw ratio from WAXS shown in figure 4 can be calibrated. The measured and calculated draw ratio from WAXS after calibration is shown in figure 6. The average draw rate is calculated from the gradient of plot.

![Figure 6](image)

Information obtained for crystallisation and local draw ratio from these type of analysis for a PET sample drawn at 90°C, draw rate 11.5 sec$^{-1}$ and to final draw ratio 3.5:1 is shown in figure 7. We have used these techniques to investigate the structural variation of PET samples at
temperature ranges from 85°C to 130°C, draw rates from 0.05 sec\(^{-1}\) to 12.0 sec\(^{-1}\) and draw ratios 1.4 to 4.7. These studies have shown that:

(i) for draw rates higher than 0.4 sec\(^{-1}\) the crystallisation begins at the end of draw and for draw rates smaller than 0.4 sec\(^{-1}\) there is evidence of start of crystallisation before the end of draw,
(ii) the level of critical orientation required for the initiation of crystallinity has an inverse relationship with the draw temperature,
(iii) once initiated, the rate of crystallisation has a direct relationship with the final level of orientation,
(iv) in studies of PET\(^9\) at high draw rates there is evidence for an intermediate structure which may be identified with the mesophase structure proposed by Windle and coworkers\(^{11}\) which persists for about 0.2 seconds immediately prior to crystallisation.

Figure 7

Recently we have extended these studies at the ESRF for biaxial drawing of PET using a modification of the Keele uniaxial drawing camera, which incorporates four, rather than two stepper motors. These motors allow various patterns of biaxial draw. The onset of crystallinity occurred approximately at the end of draw followed by gradual growth. These studies indicate that for high draw rates, detectable crystallisation does not begin until the end of draw. The rate of this crystallisation is slower than determined for uniaxial draw at the same draw rate and
temperature. Detail of this work will be reported elsewhere\textsuperscript{3}.

The power of the spatially resolved techniques, which we have developed, is demonstrated by
the study of a PET container wall. The sample was taken from near the top of the conical wall
thickness of 1 mm. X-ray diffraction data was recorded from inside to outside wall of the
container with 2.3\textmu m diameter x-ray beam in 30\textmu m steps. A selection of diffraction patterns is
shown in figure 8. These diffraction patterns were generated by point-to-point subtraction of the
last frame of the scan. Figure 8a (0\textmu m), 8b (150\textmu m), 8c (300\textmu m), 8d (420\textmu m), 8e (720\textmu m) and
8f (930\textmu m) from inside to outside of the container wall (The distance from the inside wall at
which these patterns were recorded is given in brackets).

\begin{figure}[h!]
\centering
\includegraphics[width=\textwidth]{figure8.png}
\caption{Figure 8}
\end{figure}

It can be seen from figure 8 as we move from figure 8a (inside) to figure 8f (outside) the degree
of crystallinity decreases. Figure 8a clearly shows oriented crystalline diffraction pattern and 8f
shows oriented amorphous diffraction pattern. The variation in crystallinity across the wall of the
container is shown in figure 9 by measuring the maximum peak height of two diffraction peaks.
One is along the meridional direction (I in figure 8a) and other is an off equatorial reflection (II
in figure 8a).

Conclusions form the time-resolved deformation studies of PET can be used to explain the
variation in crystallinity across the thickness of the container wall. During the industrial
production of the container, the preform made out of PET is being stretched by a plunger and
blown by compressed hot air. In this process, the outer part of the wall hits the external cold mould first and is cooled quickly, not leaving enough time to crystallise. However, in the inside of the container the drawn sample has enough time to crystallise. Therefore, the variation in crystallinity can be linked to the time-thermal history across the container wall.

**Figure 9**

**CONCLUSIONS**

A major aim of this paper has been to emphasise the impact which the advent of third generation dedicated x-ray synchrotron sources have had on the information which can be obtained on the structure of polymer materials using x-ray diffraction techniques. These applications exploit two characteristic features of synchrotron sources, *i.e.* their high intensity in the x-ray region and the very high degree of vertical collimation in the radiation emitted. These features coupled with recent advances in beam line optics for producing highly monochromatic “point” sources with cross-section dimensions of ~ 1 micron at the specimen and electronic area detectors capable of recording a 2-dimensional fibre diffraction pattern in ~ 40 msecs have dramatically extended the information which can be obtained on molecular structure and organisation within polymer materials. The high temporal resolution available has allowed changes in polymer orientation and crystallinity to be followed in response to thermal and mechanical stress comparable to that
characteristic of industrial processing. The high spatial resolution has allowed variation in polymer orientation and crystallinity as a function of position to be characterised. This ability to investigate the development and stability of structural features in polymer materials and characterisation of texture is illustrated in this paper by studies on PET but can be expected to be widely applicable in the investigation of structure/property relationships in polymer materials.

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