A method is described whereby integrated intensities can be obtained from X-ray diffraction photographs of polymeric fibres. Contour maps of optical density are produced using a digital microdensitometer and 'Photowrite' manufactured by Optronics International, Inc., and the total intensity obtained by integrating round contour lines. The method takes less time than making radial scans through the peak intensity of each reflexion arc with a scanning microdensitometer, and correcting for the spread in the circumferential direction.

Introduction

The measurement and correction of integrated intensities from X-ray diffraction photographs of polymeric fibres is complicated by three factors:

(i) reflexions are more diffuse than those from single crystals,

(ii) the fibre symmetry causes overlapping reflexions,

(iii) there is a high and variable background intensity of scattered radiation.

In early work intensities were measured by visual estimation, with the size of the reflexion taken into account, but this method has been displaced by the use of microdensitometers. A scan is taken across the centre of each reflexion arc. Background is sketched in, overlapping reflexions are apportioned, and the area under the scan of each peak is measured. Allowances must be made for the spread of the reflexion along the arc (due to disorientation in the fibre). This is done by using 'arc-correction factors' (Arnott, 1965; Cella, Lee & Hughes, 1970) which are calculated on the assumption that there is a symmetrical distribution of crystal axes about the fibre axis.

If this assumption were correct there would be a steady increase in the spread of a reflexion arc with increasing distance from the meridian along a given layer line. Inspection of Fig. 1 [taken on a fibre of poly(tetramethylene terephthalate)] shows that this is not so for this particular fibre. This material crystallizes with the polymer chain axes slightly inclined to the fibre axis, which causes the irregular layer lines. It also causes equatorial reflexions to be displaced slightly above and below the equator, though insufficiently to be resolved as distinct reflexions. They thus appear as arcs of varying elongation. Also, the reflexion arcs on non-equatorial layer lines do not increase uniformly in length with increasing distance from the meridian, though the above explanation does not apply to these. Such observations are fairly common with polymeric fibres.

It is therefore desirable to determine the integrated intensity by measuring the optical density over the entire spread of the reflexion arc and thus avoid the use of corrections for disorientation. A method of doing this is described.

Previous authors (Arnott, 1965; Cella, Lee & Hughes, 1970) have considered the correct form of Lorentz factor to use with the diffuse reflexions from polymeric fibres. This question will not be discussed here. It is a simple matter to show that, once the use of arc-correction factors has been avoided, the fibre symmetry value at the coordinates of the peak intensity of the reflexion should be applied to the integrated intensity of that reflexion. The only condition which must be satisfied is that the variation in Lorentz factor must be linear over the range of the reflexion. With oriented crystalline polymers the spread of the reflexion is usually small enough to meet this condition.

Fig. 1. X-ray diffraction photograph of oriented fibre of poly(tetramethylene terephthalate).
Development of the method

The principle of the method developed is as follows. From the diffraction photograph a contour map of each reflexion and its immediate environment is produced, the contours consisting of lines of equal optical density. From the map the level of background intensity in the vicinity of the reflexion is estimated and the area enclosed by each contour above this background is measured by planimeter. These areas are added to give the integrated intensity.

(a) Production of the contour map

First attempts to produce a contour map were made using a Joyce–Loebl microdensitometer fitted with an iso-densitracer. The microdensitometer scans along a line on the film. When the optical density passes through one of a series of critical levels the type or colour of the symbol printed by the recorder changes. The scan is repeated along a raster of lines and so a contour map is built up, the change in the type of symbol giving a contour level. Experiments were performed with two machines. One (in the Physics Department at University College, Cardiff) would print three symbols in each of three colours, the other (in the Astronomy Department of the University of Manchester) would only print in one colour.

With different colours it was found possible to distinguish contours at increments of 0.02 in optical density. Discrete contours could not be obtained at smaller increments and resolution was lost at larger ones. With a single colour, levels could not be so easily distinguished. With each machine a linear magnification of \( \times 50 \) was necessary, i.e. on a standard sheet of paper (18 × 26 cm) an area of film 3.6 × 5.2 mm was reproduced. At this magnification the separation of raster lines was 25 \( \mu \text{m} \) on the films. The aperture size in the microdensitometer was 200 \( \mu \text{m} \) square.

With this technique, satisfactory contour maps could be obtained, but the method was abandoned because it was slow. Because of the high magnification required, a complete photograph covered about 100 sheets of paper after contouring, each sheet taking about two hours to produce.

Since a series of photographs with different exposures was necessary to bring all reflexions into the correct range of optical density, it would take an impracticable length of time to scan all photographs. A much faster method has been developed, which uses a high-speed digital microdensitometer (manufactured by Optronics International, Inc.) in conjunction with an Optronics ‘Photowrite’ system.

With a digital microdensitometer (in the Biochemistry Department of the University of Bristol) optical density was recorded onto magnetic tape. This was done at points on a 25 \( \mu \text{m} \) lattice, optical densities between 0 and 2 being assigned integers between 0 and 256. The lattice size is variable, the dimension used is determined by the size of the reflexion on the film, and 25 \( \mu \text{m} \) was found to give a satisfactory number of data points for subsequent contouring. The optical density was averaged through an aperture 100 \( \mu \text{m} \) square. This size was chosen to achieve a compromise between noise due to the grain size of the film and resolution of reflexions close together. It gave a satisfactory noise level but failed to resolve a few reflexions which were distinguishable by eye.

A contour map was generated from the tape using a ‘Photowrite’ (in the Physics Department at University College, Cardiff). The operating principles of this instrument have already been described (Harburn, Miller & Welberry, 1974), though not in an application where contour lines are being plotted.

Essentially it recreates the original photograph from data on the magnetic tape. A lattice of spots is exposed onto a sheet of photographic film, each spot being exposed through a small aperture to a density proportional to the recorded optical density at its location. In the contouring mode an exposure is only made if the recorded density at that location lies within one of a series of preselected bands of optical density, and the exposure is only at one intensity. Thus, for example, the final photograph might consist of clear areas where the optical density of the original was represented on the tape by integers 0–8, 17–24 etc., and black areas where it was represented by integers 9–16, 25–32 etc. The photograph will therefore be comprised of contour lines joining points of equal optical density.

The band of optical density represented by one contour line is under the control of the operator. If it is too narrow, individual contours cannot be distinguished; if it is too broad too few contours are obtained within the linear range of the film to give a good representation of the reflexion profiles. It was found satisfactory to divide the total range of the microdensitometer into 32 levels (as in the example above).

The films were written on a 50 \( \mu \text{m} \) lattice (giving a \( \times 2 \) linear magnification of the original photograph) with an aperture size of 50 \( \mu \text{m} \). Further magnification must be achieved to produce usable maps and this is done photographically. A convenient method is to use a microfiche printer. Since black lines on a white background are all that is required, the contrast graduation of the print produced by such a machine is satisfactory, its magnification is of the correct order and it is much faster than other photographic techniques.

The time taken by the entire process depends on the size of the area of the original photograph being scanned, and the parameters chosen for the scanning and writing stages of the procedure. Typical values are 40 min to scan an 8 × 6 cm film on a 25 \( \mu \text{m} \) lattice, 20 min to write the tape produced onto a 50 \( \mu \text{m} \) lattice, and about an hour to produce a set of enlarged prints covering the areas of interest in the picture. This compares with a time of about 200 hours to produce an equivalent set of contour maps using an iso-densitracer. It is also faster than taking scans through the peak intensity of each reflexion arc with a scanning microdensitometer,
and so it becomes practical to use photographs covering a wider range of X-ray exposures than in the past and satisfactorily measure the intensities of reflexions which differ greatly.

Fig. 2 shows a contour map of the diffraction pattern of the same fibre as was used to obtain Fig. 1 (contoured at 32 levels) and Fig. 3 an enlargement of a small area of this map. The black blobs at the centres of some of the reflexions in Fig. 2 are obtained because the X-ray exposure was chosen to produce a satisfactory range of optical densities for the medium-strength reflexions. The centres of the stronger reflexions then exceed an optical density of 2, the upper limit of the wedge used on the scanning microdensitometer.

(b) Determination of integrated intensity

The most direct way to obtain the integrated intensity from the contour map of a reflexion is to decide upon the background level and to measure the areas enclosed by each contour line above this background, using a planimeter. The sum of the areas gives a number proportional to the integrated intensity. With some reflexions the background intensity changes through one or more contour levels over the area of the reflexion. In these cases the level lying halfway between the intensity of the lowest complete contour line and that of the lowest adjacent background is chosen as the mean background.

Using complete contour lines as a guide, incomplete lines at intensities above this mean background are completed. The plotting of an intensity profile aids the estimation of lowest background. Errors of judgement are likely in this procedure, but since it is seldom that more than two lines need completion their effect on the total intensity is small except for weak diffuse reflexions. Intensities can be obtained when two reflexions overlap provided their peaks are resolved. A line is drawn through the centre of the reflexion in a direction such that the intensity contours on one side of this line are undistorted by the overlap. The areas between the intensity and this line are measured in the undistorted part. Intensities cannot be obtained where the peaks of overlapping reflexions are not resolved, or for the centre of three overlapping reflexions.

The method described is a satisfactory way of determining integrated intensities, but is laborious and time-consuming. If it is assumed that the intensity profiles of different reflexions differ only by scaling factors then it is not necessary to measure the area enclosed by all contour lines. It is sufficient to measure only the one lying at an intensity mid-way between that of the peak and the background and multiply this by the number of contour levels within the reflexion. A set of numbers proportional to the integrated intensities is thus obtained with a considerable saving of labour over the other method.
In both methods it is assumed that background and peak intensity lie exactly in the middle of the intensity band represented by their contour-level. Since they may lie anywhere in the band there is an uncertainty of \( \pm 1 \) contour level. If the contour map is printed with 32 levels in the optical-density range of the scanning microdensitometer (0–2) there are 16 levels in the linear range of the film. If a series of diffraction photographs is taken differing in exposure by a factor of two, then all but the very weakest reflexions will appear on one photograph with at least eight contour levels. The error in the measurement of the intensity will therefore be about \( \pm 12\% \). With the very weakest reflexions which appear on the longest-exposure diffraction photograph with only one or two contour levels the error is likely to be considerably greater. This is also true for overlapping reflexions and those in regions of rapidly varying background. It is worth printing the contour map of the photograph with the longest exposure at 64 levels as well as at 32, to reduce the error in the intensity of these very weak reflexions. (At 64 levels it is not possible to distinguish individual contour lines on reasonably strong reflexions.)

Results

As an example of the use of the method the intensities of three reflexions from a diffraction pattern of the material used to obtain Fig. 1 have been measured in the conventional manner using arc-correction factors and using the contouring method described here. Values have been obtained both by measuring the areas enclosed by all contour lines, and by measuring that enclosed by the mid-intensity contour. All of these measurements have been made on photographs differing in exposure by factors of two. The results are given in Table 1. To facilitate comparison, intensities have been divided by the length of exposure, and standardized to a scale in which the 40 min exposure of reflexion No. 3 has a relative intensity of unity. Reflexion No. 1 was isolated and Nos. 2 and 3 overlapped slightly.

Table 1. Comparison of relative intensities obtained by different methods

<table>
<thead>
<tr>
<th>Reflexion No.</th>
<th>Exposure (min)</th>
<th>All contours measured</th>
<th>Mid-intensity contours measured</th>
<th>Arc-correction factors used</th>
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<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>0.90</td>
<td>1.00</td>
<td>0.98</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.98</td>
<td>1.04</td>
<td>0.94</td>
</tr>
<tr>
<td>2</td>
<td>160</td>
<td>0.080</td>
<td>0.117</td>
<td>0.121</td>
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<td></td>
<td>320</td>
<td>0.078</td>
<td>0.107</td>
<td>0.106</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>0.86</td>
<td>0.99</td>
<td>0.96</td>
</tr>
<tr>
<td></td>
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<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
</tr>
</tbody>
</table>

It can be seen from an inspection of the results for the two longer exposures with reflexion 3, that good agreement is obtained between different exposures, provided adequately exposed photographs are used. The results for the 10 min exposure indicate the growth in error when exposure is such that too few contour lines are obtained.

Fig. 3. Enlargement of a small area of Fig. 2.
The agreement between the two contouring methods for the relative intensities of reflexions 1 and 3 is within the possible error previously estimated. Comparison of the two methods for reflexion 2 shows how error increases for a weak overlapping reflexion.

The relative intensities obtained with an arc-correction factors lie slightly, but not significantly, outside the range of values obtained by the two contouring methods. It would require more extensive investigation to indicate possible errors caused by the use of these factors.

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References