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Full-pattern parametrization of two-dimensional wide-angle diffraction data from oriented polymers

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Two-dimensional wide-angle X-ray scattering data from oriented polymers are profile fitted by describing the intensity distribution as a product of two orthogonal functions in polar cylindrical coordinates. The parameters of the fit are used to describe the structure in terms of amorphous and crystalline orientation, crystallinity and crystallite size. The possibility of using the data to refine the unit cell parameters and the atomic coordinates is discussed. The analysis is illustrated with data from a nylon 6 fibre, and the results are compared with those from a previous analysis of a series of one-dimensional scans. The method is compared to alternative modelling approaches such as Rietveld refinement. © 1997 Elsevier Science Ltd.

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Introduction

X-ray diffraction (XRD) data from polymers are routinely obtained as one-dimensional (1-D) scans and analysed using the now commonly available curve fitting computer programs. These 1-D results are adequate for the analysis of unoriented samples. However, 2-D data are necessary for analysing oriented specimens, which require determination of amorphous and crystalline orientation, evaluation of crystallite sizes in different directions, and the determination of unit cell parameters and atomic coordinates. The 2-D data can now be collected rapidly using area detectors or can be assembled from a series of scans obtained from 1-D detectors. The limiting step has been the analysis of the 2-D data. We here propose and illustrate a method for analysing such 2-D data using a full-pattern least-squares analysis.

The two methods for analysing wide-angle X-ray diffraction (WAXD) are refinement of a model to fit the data and parametrization of the data using profile fitting. Rietveld refinement of 1-D powder diffraction data perhaps best illustrates the method of fitting a structural model to the data. Busing has extended this method for analysing 2-D data[1], which has also been used by Fu and Wunderlich[2–4]. This method requires that the details of the model, such as atomic coordinates and a description of the various disorders, be known *a priori*. Parametrization of the data requires no prior knowledge of the structure, and hence is routinely used in industry to characterize, compare and contrast unknown polymers. We have been using this approach for analysing 1-D WAXD data[5–8]. The data are least-squares fitted to various peaks, and the parameters of the fit (the position, amplitudes and the widths of the peaks) are used to calculate a set of generic parameters such as orientation, crystallinity and crystallite size. We here extend the parametrization method to 2-D WAXD data.

Data analysis

Data from 4.5× drawn nylon 6 fibre will be used to illustrate the method. XRD data were collected in $\theta/2\theta$ mode on a Philips diffractometer using CuKα radiation with a graphite monochromator in the diffracted beam. Twenty-three radial scans were obtained in two quadrants (azimuthal angles ϕ between -90 and $90°$) by rotating the sample by 5–10° between successive radial scans. The series of 1-D WAXD radial scans were assembled into a 2-D matrix, which is shown in *Figure 1a*.

The function used to describe 2-D data should be separable into independent functions along the coordinate axes. This is readily achieved in the wide-angle case by choosing polar cylindrical coordinates. In the equations given below, u and v are the coordinate axes, u is the scattering angle 2θ and v is the azimuthal angle ϕ. The coordinates are chosen so that the intensity $I(u,v)$ at a given point (u,v) can be described as a product of two independent (i.e. orthogonal) functions $f(u)$ and $g(v)$ in the form

$$I(u,v) = I(0,0)f(u)g(v) \qquad (1)$$

where $I(0,0)$ is the amplitude of the peak. Analysis of the radial scans in the WAXD data showed that our data can be best described by modified Lorentzians. We also explored different peak shapes for both the u and v axes, and found that modified Lorentzians best describe our data. Changes in the peak shapes are not likely to influence the final results described in this paper. Modified Lorentzian functions are Pearson VII functions with the shape factor $m = 2$, and are given by the relation

$$F(x) = F(x_0)/(1 + kx^2)^m \qquad (2)$$

$$k = (2^{1/m} - 1)/(fwhm)^2 \qquad (3)$$

where $fwhm$ is the full-width at half-maximum. We used the following expressions in analysing the data from

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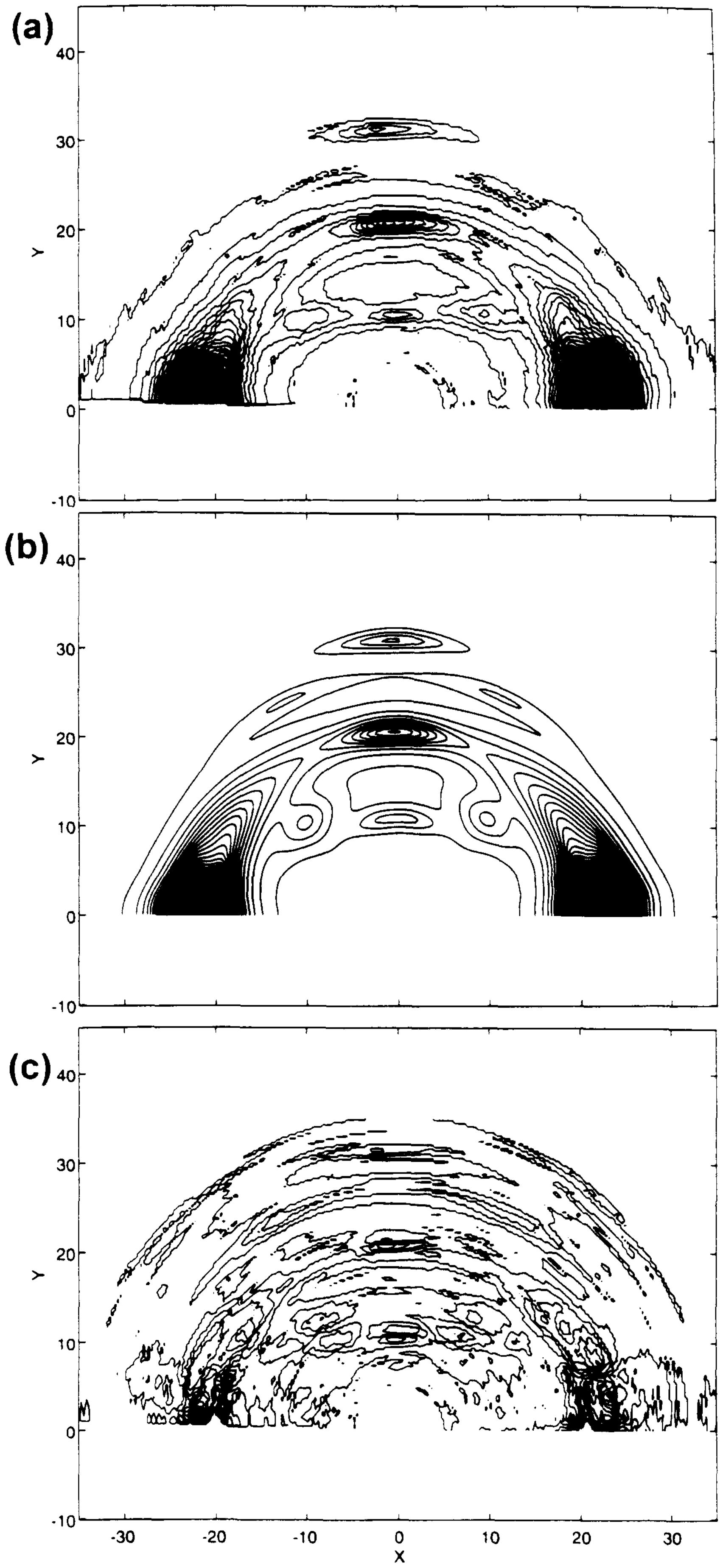

Figure 1 Contour map of the wide-angle intensity distribution of the 4.5× drawn nylon 6 fibre. (a) Observed data. (b) Fitted data. (c) Difference map. The x and y axes are marked in degrees. The fibre-axis (y axis) is vertical

cylindrically symmetric fibres:

$$f(u) = 1/(1 + (k(u - u_o)/u_w)^2)^2 \quad (4)$$

$$g(v) = (g_1(v) + g_2(v) + g_3(v) + g_4(v))/4 \quad (5)$$

$$g_i(v) = 1/(1 + (k(v - v_i)/v_w)^2)^2 \quad (6)$$

$$v_1 = v_o \quad (7)$$

$$v_2 = 180 - v_o \quad (8)$$

$$v_3 = 180 + v_o \quad (9)$$

$$v_4 = 360 - v_o \quad (10)$$

The subscripts o and w refer to the position and the width of the peaks, respectively. The four functions of g generate the same features in each of the four quadrants. The four quadrants are identical in the diffraction patterns of oriented polymers. During the least-squares calculations, to ensure that the intensities up to only $\pm 180^\circ$ in ϕ on either side of the peak maximum are included in the calculations, 360° is subtracted from $v - v_i$ when $v - v_i > 180^\circ$, and 360° is added to $v - v_i$ when $v - v_i < -180^\circ$. The least-squares fit was carried out using the DN2FB subroutine in the AT&T NETLIB library[9].

The number of functions used to describe the WAXD patterns depends on the complexity of the diffraction pattern. In the example used here, the data are described by four equatorial functions ($\alpha_1, \alpha_2, \gamma_1$ and γ_2), three meridional functions (020, 040 and 060), four layer line functions (layer lines 1–4), and two functions describing the amorphous intensity (isotropic and anisotropic components)[6,8]. The orientation of the various reflections is related to the azimuthal width $\Delta\phi$, and the crystallite sizes can be obtained from the radial width $\Delta(2\theta)$ using the Scherrer equation[10]. A crystalline index (CI) is calculated from the expression

$$CI = A_c/A_t \quad (11)$$

where

$$A_t = A_c + A_a \quad (12)$$

A_t, A_c and A_a are, respectively, the areas under the entire scattering curve, the crystalline peaks and the amorphous components. These are obtained by integrating the intensity according to[11]

$$A = \int_{r_{\min}}^{r_{\max}} \int_0^{\pi/2} I(r, \phi) \sin\phi \, d\phi \, dr \quad (13)$$

using the total intensity I_t for calculating A_t, the crystalline peak intensity I_c for A_c and the intensity of the amorphous halo I_a for A_a.

In the above calculation of the crystallinity, it is necessary to resolve the observed pattern into crystalline and amorphous contributions. The crystalline and amorphous peaks were separated on the basis of a diffraction pattern from a reference sample consisting of large crystallites, which provides clearly identifiable crystalline peaks[5]. We have recently been pursuing an alternative idea in which instead of identifying the peaks as crystalline and amorphous, each peak is assigned a weight which determines the extent to which a peak could be regarded as crystalline. This weight, $W(b_i)$, depends on the width b_i of the peak which is determined by the coherence length or the crystallite size of the scattering entity. The weighted crystalline index (WCI) is calculated from the expressions

$$WCI = \left[\sum A_i W(b_i)\right] / \left[\sum A_i\right] \quad (14)$$

$$W(b_i) = \exp -[b_i/\Delta(2\theta)_c]^2 \quad (15)$$

A_i is the area of a peak and b_i is its width. $\Delta(2\theta)_c$ is the critical or the cut-off value of the full-width at half-maximum of the peak, and is used to separate the crystalline peaks from the amorphous halo. Our experience has shown that an appropriate value for $\Delta(2\theta)_c$ is 4.3° for analysing nylon 6. Implicit in the choice of this value is the assumption that all domains which are much larger than 20 Å in size should be considered as crystalline, those which are much less than 20 Å be considered as amorphous, and those in the vicinity of 20 Å will be weighted depending on how close they are to the cut-off value. Thus, the commonly accepted broad amorphous halo will be considered as amorphous, and the clearly defined crystalline peaks are considered as crystalline, but the peaks which are ambiguous will be assigned a weight which increases with the increase in the crystallite size. In addition to eliminating the need for amorphous standards, this procedure also takes into account the microcrystallites and apportions them to crystalline fractions depending on the size of the crystallites.

Results and discussion

Figure 1 illustrates the analysis of WAXD data. *Figures 1a* and *1b* are the contour maps of the intensity distribution in the observed and the fitted data for the 4.5× drawn fibre. The difference between the observed and the fitted data is plotted in *Figure 1c*. The parameters which describe *Figure 1b* are shown in *Table 1*. Some of the commonly used fibre parameters such as crystallinity, index of crystalline perfection, $ICP = 2\theta(\alpha_2) - 2\theta(\alpha_1)$, and 2θ and the ϕ width of the frequently used reflections are compared in *Table 2* with the values obtained in our previous analysis of the same data as a series of 1-D scans[8]. The agreement between the old and new sets of results is quite satisfactory given the quality of the data, except for the value of fractional amorphous orientation. The fractional amorphous orientation, defined as the ratio of the area of the oriented amorphous peak to the total amorphous scattered intensity, was measured in our previous analysis from a single azimuthal scan of the amorphous intensity. In the present analysis, the ratio is determined by the total 2-D area. This can account for the large difference obtained by the 1-D and the 2-D methods. The present analysis is much faster (hours compared to days) and accurately reflects the complete XRD data. *Table 2* shows that the two crystallinities, CI and WCI, are the same for this particular sample. In general, however, the two values are not expected to be the same.

In the method proposed here, we first parametrize the amorphous and crystalline intensities. These parameters are then used in further calculations such as the degree of order (density and orientation) in the amorphous regions, and the disorder in the crystalline regions. Since the crystalline peak parameters are derived after removing the amorphous scattering, the data can be readily used, if necessary and feasible, for refining unit cell parameters and atomic coordinates. The method described here is useful in an industrial setting for

Table 1 Parametrization of the WAXD data from a drawn nylon 6 fibre using 13 2-D functions. Base line = 312.35, slope = 0.538, ϕ offset = −1.36, residual error = 0.284

Label	2θ	ϕ	2θ *fwhh*	ϕ *fwhh*	Amplitude
Alpha #1	20.12	3.34	1.47	8.63	19 861
Alpha #2	23.30	3.25	2.38	9.03	26 423
Gamma #1	20.56	0.65	1.86	9.41	3 997
Gamma #2	22.92	1.90	1.17	7.65	999
020	10.84	80.00	2.22	28.97	1 036
040	20.58	85.79	2.02	20.10	2 000
060	30.91	87.38	1.62	17.56	955
Layer line #1	14.37	46.86	4.27	23.97	1 679
Layer line #2	20.76	28.67	3.30	20.00	999
Layer line #3	19.66	11.93	2.22	7.10	2 402
Layer line #4	26.97	64.15	1.69	29.50	795
Oriented amorphous	22.53	1.48	4.33	31.14	2 969
Unoriented amorphous	20.28	0.17	4.98	84.14	2 020

Table 2 Comparison of 1-D and 2-D analysis of WAXD data

Parameters	1-D analysis	Full-pattern refinement
Crystallinity (%)	47	47
Weighted crystallinity (%)		46
ICP (degrees, $2\theta_{\alpha 1} - 2\theta_{\alpha 2}$)	3.16	3.23
Crystallite size (2θ width in degrees)		
$\alpha 1$	1.3	1.47
$\alpha 2$	2.48	2.38
$\gamma 1$	1.99	1.86
$\gamma 2$	1.35	1.17
020	1.27	2.02
040	1.51	2.22
Oriented amorphous peak	4.5	4.33
Orientation (ϕ width in degrees)		
$\alpha 1$	13.8	8.63
$\alpha 2$	14.3	9.03
Oriented amorphous peak	38	31
Fractional amorphous orientation ($A_{oa}/(A_{oa} + A_{ua})$)	0.49	0.19

characterizing and comparing polymers from limited intensity data (as little as 5–35° 2θ with CuKα radiation ($\lambda = 1.54$ Å) as in *Table 1*) when we know little about the material. The diffraction pattern is described by a set of physically meaningful parameters such as size, orientation and disorder (*Table 2*) without making any assumption about the structure giving rise to the features in the diffraction pattern. These parameters may be sufficient for most practical applications even when the details of the structure, which enable the calculation of atomic coordinates and the details of the structural disorder, are known.

Thus, at one extreme we have the method described here in which, starting from the data, we arrive at a set of parameters which describe the structure. At the other extreme, which is best represented by the 2-D Rietveld refinement for the case of WAXD, we start with a structural model and refine the model to fit the data. In the first method, we run the risk of losing the structural insight which we might obtain if we had a model. In the second instance, the results of the refinement are only as good as the model. For instance, by fitting a model with a single crystalline phase to the data from extended chain polyethylene, Busing suggested that the residual scattering at 20° 2θ between the observed and the calculated intensities is due to the wandering of the polymer chains from one ordered site to the next along the *b* axis[1]. But, using the approach described here, this intensity could be attributed to the presence of up to 20% of a highly oriented amorphous or non-crystalline fraction[7]. Each of these methods has its own strengths and weaknesses, and the method to be used depends on the problem and the resources on hand.

Conclusion

Full-pattern refinement of 2-D data is the most efficient and appropriate method for analysing diffraction patterns from oriented polymers. WAXD data can be analysed using polar coordinates, and generic parameters such as crystallinity, orientation and crystallite size can be readily obtained. A tentative proposal for determining the crystallinity of a semicrystalline polymer without explicitly defining the amorphous halo is presented.

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