An empirical estimation of Scherrer parameters for the evaluation of true crystallite size in fibrous polymers

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Optical diffraction profiles obtained from computer-drawn masks which simulate the effects of both size and distortion, have been used to evaluate Scherrer (K) parameters in terms of the ratio of true crystallite size to apparent crystallite size. These empirical parameters are in reasonable agreement with parameters established by comparing the results of X-ray and electron diffraction analyses with direct measurement on lattice–fringe images. Tables are given for K parameters to be used in the evaluation of true crystallite size from the integral breadth or half-width of diffraction profiles.

INTRODUCTION

The measurement of crystallite size in fibrous and other polymers is of considerable importance, particularly with respect to changes of structure which take place during processing and after exposure to heat, light, or chemical agents. Crystallite size measurements may be obtained from X-ray diffraction patterns by the evaluation of peak broadening, a procedure which is complicated by effects due to lattice distortion and crystallite-size distribution, and by the absence of strong higher orders. It is often convenient to estimate an 'apparent' crystallite size from a first-order reflection; this can be a most useful measure, but it is far from clear how the apparent crystallite size relates to the true crystallite size.

Size broadening is usually evaluated by means of the Scherrer formula

$$L_{hkl}=\frac{K\lambda}{\beta\cos\theta}=\frac{K}{\Delta s}$$

where L_{hkl} is the apparent crystallite size measured either from β_I, the integral breadth of the profile, or β_W, the half-height width, usually referred to as the half-width. Δs is the integral breadth or half-width of the profile in terms of s, the reciprocal lattice vector $2\sin\theta/\lambda$. The Scherrer parameter, K, is best defined as the ratio by which the apparent crystallite size must be multiplied to obtain the true size, i.e.

$$K=\frac{\text{True crystallite size}}{\text{Apparent crystallite size}}$$

K is usually considered to have the values 1.0 for integral breadth and 0.89 for half-width; however, it has been shown that different shapes of cubic crystals will give rise to different K values[1]. There have also been several theoretical considerations of the most appropriate K values for the two-dimensional *hk* reflections from turbostratic forms of graphite[2,3]. It is generally understood that, in terms of three-dimensional *hkl* reflections, the size of the crystallite will affect the Scherrer parameter, but as yet, no quantitative estimates have been obtained, mainly because there has been no reliable evidence for estimating true crystallite size. Consequently, despite the known limitations, K parameters of 1.0 or 0.89 are universally applied to estimate size broadening in fibrous polymers.

Recently, as a result of advances in the technique of high-resolution electron microscopy, it has been possible to resolve lattice–fringe images from several inorganic materials, and, despite their sensitivity to the electron beam, from some organic materials. In this laboratory we have successfully obtained lattice–fringe images from Type I carbon fibres[4] and from poly(*p*-phenylene terephthalamide) (PTT) fibres[5]; from these images we have obtained crystallite size distributions and hence measures of true mean crystallite size. Granted there is no exact one-to-one correspondence between lattice fringes in an image and lattice planes in an object, and moreover it has been shown that reversals in the phase-contrast transfer function for the electron microscope may cause information gaps in the image at certain levels of defocus[6,7]. Nevertheless, at the optimum focus levels, it is possible to record meaningful and valid lattice–fringe images for quantitative examination and evaluation of crystallite size parameters including true mean size.

In theoretical discussions of profile broadening it is usually recognized that the contribution of distortion broadening must be taken into account, in practice the

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effect on the Scherrer parameter is neglected, and the varied methods used to separate the size and distortion contributions to profile broadening (see for example Buchanan and Miller[8]) assume that $K=1$. Hosemann and his colleagues[9,10] introduced and promulgated the concept of paracrystallinity in polymers. They showed how simple point lattice masks could be used in an optical diffractometer to illustrate the ideas of both short-range disorder, which gives rise to the so-called distortion of the first kind, and of long-range disorder, which gives rise to distortion of the second kind. From a theoretical standpoint, distortion of the first kind is held to give a reduction in height of successive diffraction peaks without change in breadth, whereas distortion of the second kind is held to give an increase in breadth together with a reduction in amplitude. Despite the advent of the laser and the widespread use of the optical diffractometer in teaching and research, there does not appear to have been any further investigation of the effect of lattice distortion on the optical transform.

It was the purpose of this current work to investigate, using methods analogous to those used in X-ray or electron diffraction analysis, optical transforms from computer-drawn, two-dimensional masks which simulate lattice–fringe images of crystallites with a known size and with known amounts of lattice distortion. By evaluating crystallite size from the optical transforms, empirical K parameters can be obtained. K parameters can also be determined by a comparison of mean size measured in lattice–fringe images, and apparent crystallite size evaluated by X-ray or electron diffraction methods. The two sets of K parameters should give some further insight into the validity of the K values commonly applied.

EXPERIMENTAL

A computer program was written in ALGOL 60 for the purpose of drawing analogue lattice fringes on a Calcomp incremental plotter run via the Leeds University 1906A Graphical Scheme SPECTRE. A line grating is drawn in which the line spacing may be varied, different crystallite sizes may be output, and lattice distortion may be incorporated. The distortion, which is essentially that of the first kind, is produced by dividing each lattice line into 100 points, then displacing each point laterally by a number of plotter steps so that the displacements form a Gaussian distribution with a calculated rms value in terms of the lattice spacing. Each line has a different displacement pattern as produced by a randomizing procedure.

Initial experiments showed that the best masks to simulate lattice–fringe images had sinusoidal density variations with low optical density (around 1.0D). All masks were reproduced on film by a standardized method and were mounted without glass in standard frames. Optical transforms of the masks were observed and recorded in a Polaron optical diffractometer incorporating a 1 mW He–Ne laser providing a source of coherent light of wavelength 632.8 nm. Additional apparatus was designed to rotate the mask in the beam in order to simulate complete disorientation of the crystallites. The optical diffraction profiles were traced on a Joyce–Loebl microdensitometer and the peaks and background separated by our standard computational method, used for profile resolution in X-ray diffraction traces from several fibrous polymers[11–15]. With this method, each profile is fitted to a function of the form

$$I=fG+(1-f)C$$

where G is the Gaussian function

$$y=A\exp\left[-\ln 2\left\{\frac{2(X-P)}{W}\right\}^2\right]$$

and C is the Cauchy function

$$y=A/1+[2(X-P)/W]^2$$

with A the peak height, P the peak position, and W the peak half-width. The profile-function parameter f has been described earlier[14]; when it has the value 1, the profile is Gaussian, when it is 0, the profile is Cauchy. In general we have found that $-0.5<f<1$ for a variety of peak profiles.

After smoothing by profile resolution, the peaks were converted from arbitrary units into optical density using the given densitometer wedge calibration; they were then converted into intensity data in terms of the response of the photographic emulsion to the He–Ne source, as determined in a subsidiary experiment, then refitted to a final Gaussian–Cauchy function as before. In order to correct for instrumental broadening, which will include any broadening due to rotational inaccuracies, we have made use of a photographic reproduction of a 150 line grating drawn on a Bridgemont milling machine fitted with a pen[16]. This grating, which simulates an infinite crystal, being greater than the diameter of the incident beam, gave 17 orders of diffraction. After rotation of the grating, the profile of the first order was smoothed and corrected as described above; this profile was then used as the standard profile to correct the intensity profiles by means of a Stokes deconvolution procedure. After correction for instrumental broadening, the apparent crystallite sizes were evaluated from both half-width and integral-breadth measurements, then compared to the known real crystallite sizes to obtain the empirical Scherrer K parameters.

RESULTS

Initial experiments

Three trial masks and the first-order reflections in their optical transforms are illustrated in *Figure* 1. The line width and spacing were identical, hence even orders of diffraction are missing. *Figure* 1*a* is the analogue of a large perfect crystallite and gives a sharp peak with an approximately Gaussian profile. *Figure* 1*b* shows the effect of having a number of smaller crystallites of equal size; the first order reflection is broadened and secondary maxima appear. When the crystallites are not of equal size, the secondary maxima tend to overlap, as is illustrated in *Figure* 1*c*. This effect in a diffraction profile from a real distribution of crystallites will tend to give it a more Cauchy-like nature.

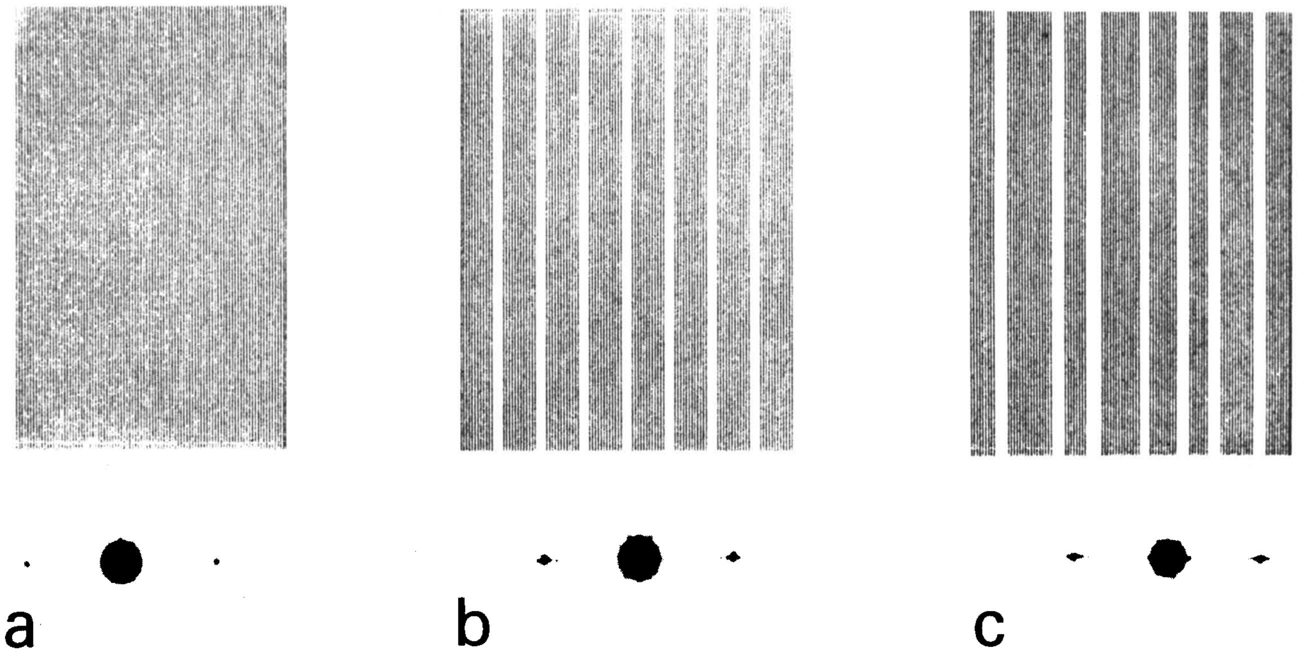

Figure 1 Trial masks and their first order optical transforms: (a) large crystallite; (b) small crystallites of same size; (c) small crystallites of different sizes

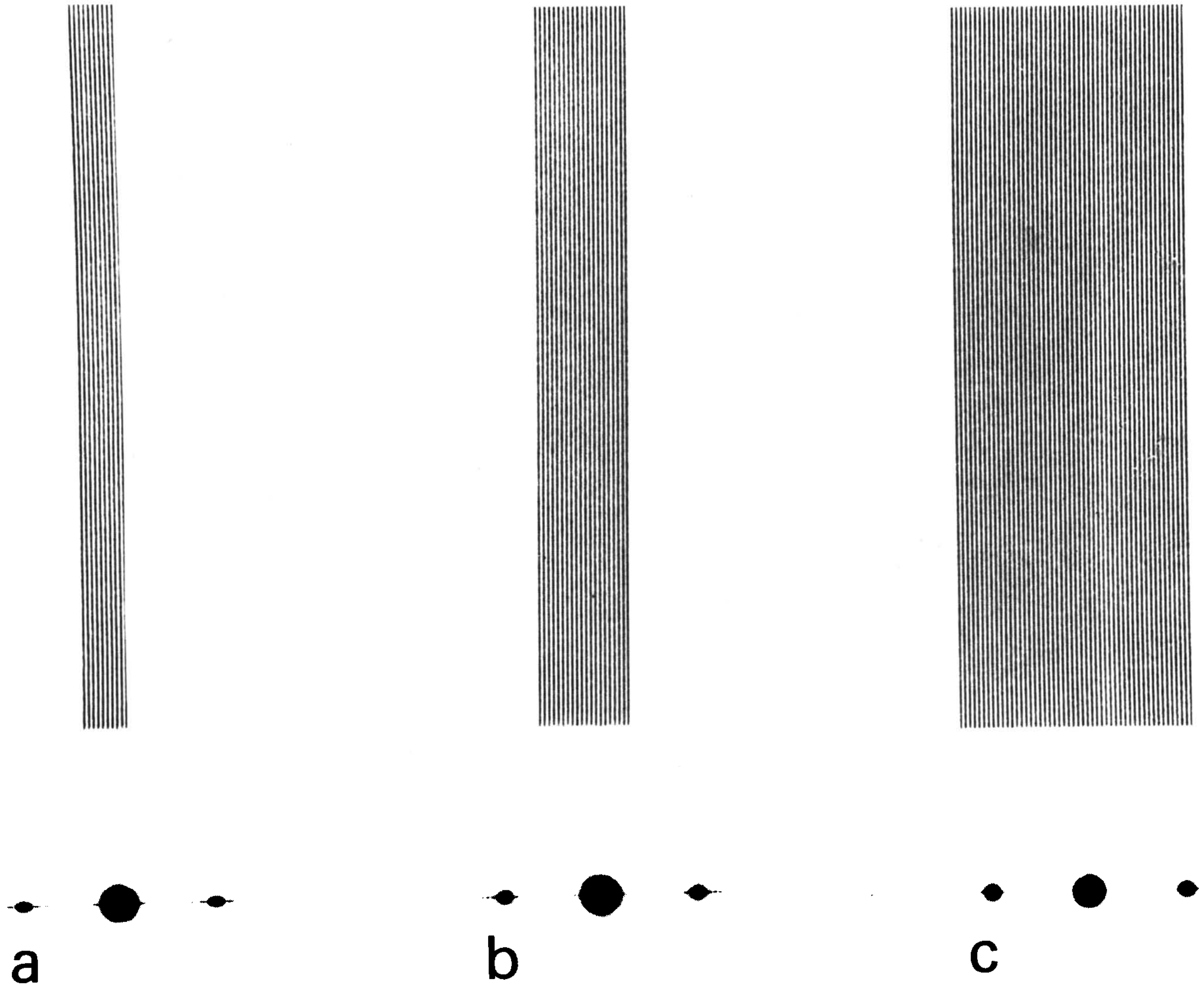

Figure 2 Masks of different sized crystallites (no distortion) and their first order optical transforms: (a) 10 lines; (b) 20 lines; (c) 50 lines

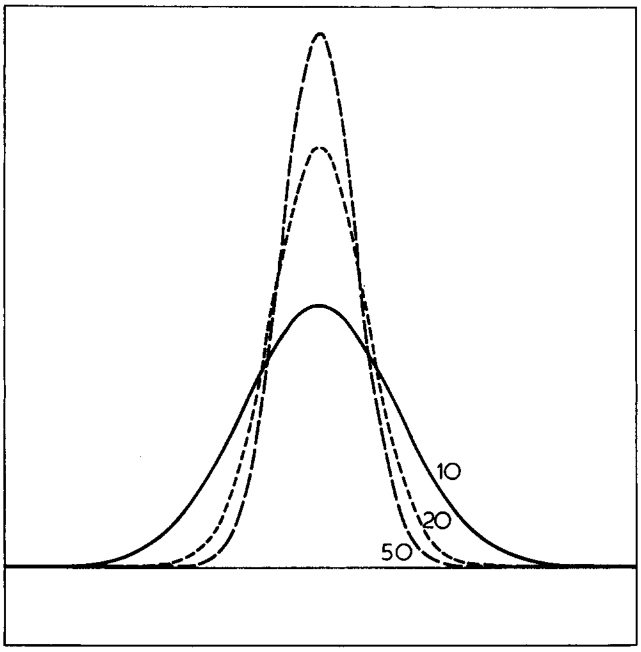

Figure 3 First order profiles of rotated masks shown in *Figure 2*

Variation of crystallite size

A series of masks was prepared with perfect lines between 10 and 50 in number; three masks with 10, 20, and 50 lines, are illustrated in *Figure* 2 together with their optical transforms. The optical transforms from rotated masks are analogous to powder diffraction patterns and were recorded so that the optical density of each first order reflection was less than one. After correction and analysis as described above, all profiles were found to be approximately Gaussian in shape and to show the expected sharpening as the number of lines in the mask increased. Three profiles normalized to standard area are shown in *Figure* 3. The values of corrected integral breadth I_B, apparent crystallite size L_A (evaluated with $K=1$), and true crystallite size L_T, are given in *Table* 1. The Scherrer parameter for size broadening $K_{S'}$ required to equate L_A and L_T, is also included. The best-fit parameter K_S increases according to the relationship

$$K_S = 0.495 + 0.009N + 3.3\ 10^{-4}\ \mathrm{N}^2 - 3.2\ 10^{-6}\ \mathrm{N}^3$$

where N is the number of simulated lattice lines. Values of K_S for half-width are always slightly lower, for example 0.5 for 10 lines, and 1.31 for 50 lines.

Variation of lattice distortion

After several trials, a series of masks with 100 lines was prepared having lattice distortion in the range 0–10%. *Figure* 4 shows masks with 4 and 8% distortion together with their optical transforms. Although the line width and spacing are not equal, the distortion of 4% produces a mask which is a realistic analogue of the lattice–fringe images seen in high-resolution electron micrographs of high-modulus fibres. After rotation, the diffraction patterns were recorded, then first order profiles were corrected and analysed as before. Smoothes profiles normalized to standard area are shown in *Figure* 5. The results of the quantitative analysis are given in *Table* 2. It is evident that the increase in distortion causes decreases in:

(i) the number of orders of diffraction,
(ii) the profile–function parameter f, and
(iii) the apparent crystallite size.

The Scherrer parameter for both 100 line size and distortion broadening increases with distortion and is given as K_D in *Table* 2.

Scherrer parameters for size and distortion broadening

Each of the diffraction profiles studied here can be considered as a convolution of a size-broadening profile and a distortion-broadening profile. In order to find the effect of lattice distortion alone on the 100 line masks, a deconvolution procedure was applied in which the 0% distortion profile, that is the 100-line size-broadening profile, was unfolded from each of the other distortion profiles. The result of this operation on the 10% distortion profile is shown in *Figure* 6.

The pure distortion profiles were then folded with the size-distortion profiles by means of a convolution procedure which also gives the resultant integral breadths and half-widths. Scherrer parameters for both size and distortion (K_{SD}) were then evaluated and are given in *Tables* 3 and 4 for integral breadth and half-width respectively. Real crystallites in fibrous polymers generally have stacking sizes between 10 and 50 layer planes in width, consequently, apart from very exceptional materials, these parameters should have widespread application.

Validity of empirical parameters

In order to test the validity of this empirical set of parameters, recourse must be made to K parameters evaluated from real materials. For this purpose we have available the measurements made from lattice–fringe images of carbon fibres[4] and PPT fibres[5], as discussed earlier, and in addition, lattice–fringe image measurements from a highly ordered carbon whisker[17] and a relatively disordered carbon fibre[18]. In all cases either or both X-ray and electron diffraction estimates of apparent crystallite size have been obtained following conventional methods. The results are set out in *Table* 5.

Of the two values of crystallite size given for the lattice–fringe measurements on Type 1 carbon fibre (2500°C), that of 3.5 nm relates to the mean value from a dark-field (002) image of the 0.34 nm lattice planes, and the value of 4.5 nm relates to the mean value from a bright-field image. Although there will be a few crystallites not sampled by the dark-field aperture, many small crystallites at various angles to the fibre axis are not seen in the bright-field mode because of

Table 1 Variation of K with lattice size, instrumental breadth 0.004°

Number of lines	Corrected integral breadth $I_B(2\theta)^0$	Apparent crystallite size L_A (mm)	True crystallite size L_T (mm)	$K_{S'}$	K_S
10	0.0210	1.72	0.95	0.55	0.62
15	0.0188	1.93	1.48	0.77	0.70
20	0.0131	2.77	2.01	0.73	0.79
25	0.0125	2.89	2.54	0.88	0.89
30	0.0124	2.92	3.07	1.05	0.99
50	0.0103	3.53	5.19	1.47	1.40

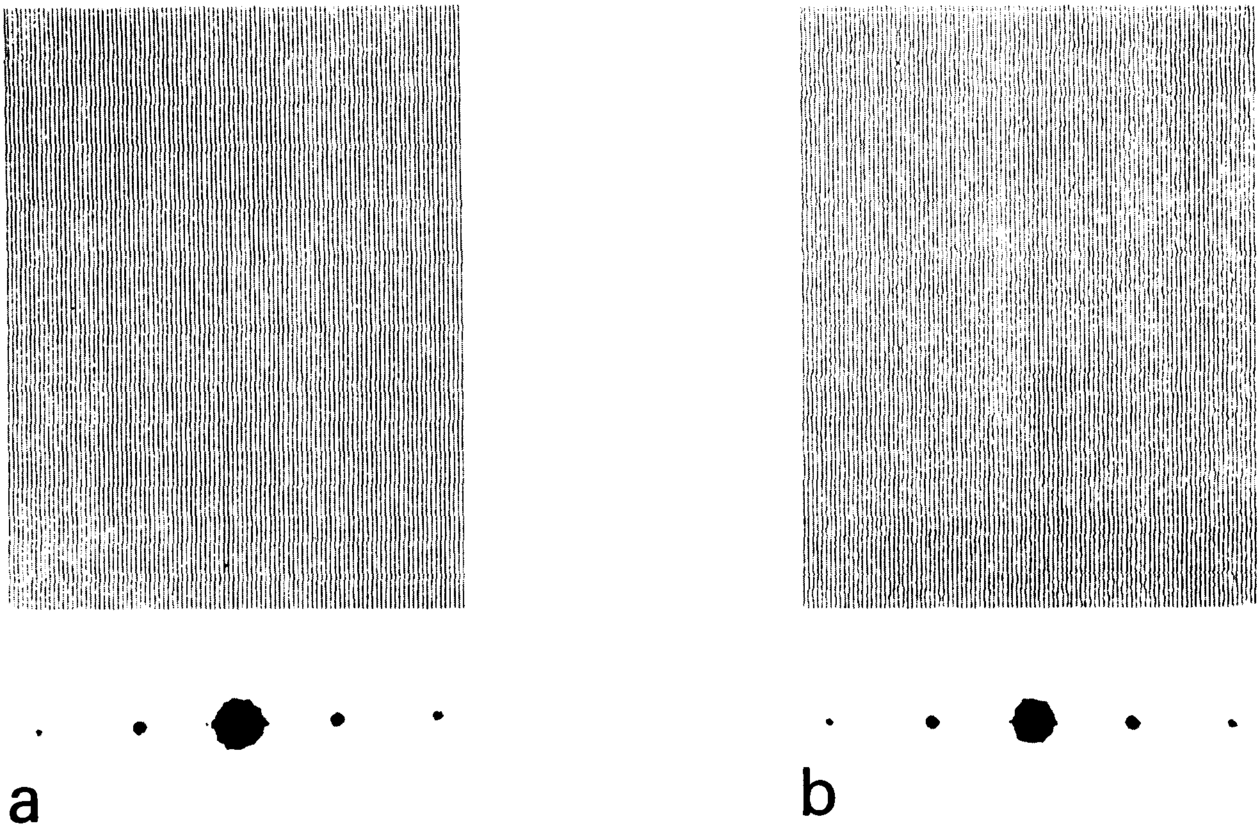

Figure 4 Masks with 100 lines and distortion of a, 4%; b, 8%

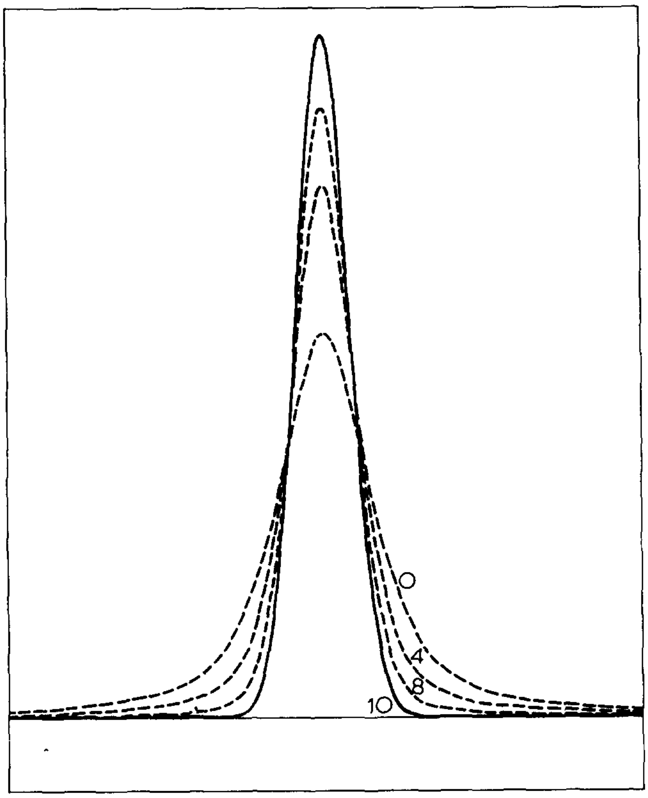

Figure 5 First order profiles of rotated distortion masks (100 lines), 0, 4, 8, 10% distortion

low contrast[4]. The apparent crystallite size of 5.2 nm in electron diffraction, comes from an equatorial trace excluding crystallites at angles to the fibre axis, the value of 4.3 nm is obtained from a procedure designed to include crystallites at high angles to the fibre axis[4].

Table 2 Variation of K with distortion, instrumental breadth 0.004°, real crystallite size 8.30 mm, number of lines 100

Distortion (%)	Number of orders	f	Apparent crystallite size (mm)	K_D
0	9	1.0	5.41	1.53
4	4	0.8	4.81	1.72
8	3	0.5	4.23	1.95
10	2	0.3	3.04	2.70

The appropriate K parameters are therefore 3.5/4.3 =0.8 and 4.5/5.2=0.9. The X-ray diffraction value of 3.8 nm relates to a rotated specimen and the value of 5.1 nm to an equatorial trace. The most appropriate K parameters are 3.5/3.8=0.9 and 4.5/5.1=0.9. The distortion has been estimated as 3%[17], thus, from *Table* 3, using 11 or 14 lattice lines we anticipate K_{SD} parameters of 0.7 or 0.8.

The same exercise carried out on PPT fibres yields K parameters of 0.7 for the ratio of image size to electron diffraction size, and 0.8 for the ratio of image size to X-ray diffraction size. The empirical K_{SD} parameter based on a measured distortion of 1.5%[18] is 0.7. For the carbon whisker we find a ratio of lattice-fringe size to electron diffraction size of 1.5 and from *Table* 4, 45 lattice lines and zero distortion[17], a K_{SD} value of 1.3. In terms of the Type A carbon fibre (1000°C) a K parameter of 1.1 is obtained from the ratio of the lattice-image size to the X-ray diffraction size, and a K_{SD} parameter 1.0 from *Table* 4. The distortion in this specimen cannot be measured by conventional methods because only one diffraction order is available and we must assume that the disorder is greater than 10%.

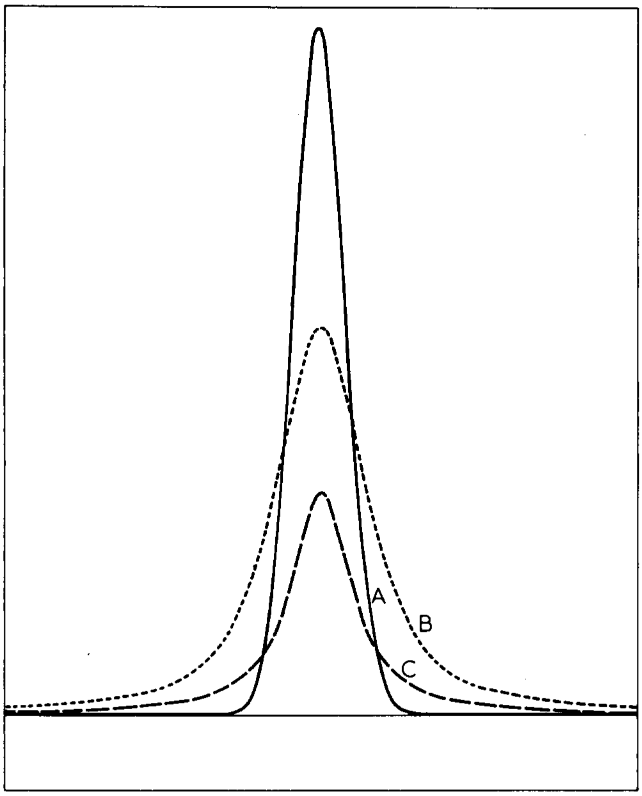

Figure 6 Effect of unfolding 0% distortion (size only) profile A, from 10% distortion profile B, to give distortion-only profile C

Table 3 Values of K due to combined effects of size and distortion K_{SD} (Integral breadth)

Distortion % Number of layer planes	0	4.0	8.0	10.0
10	0.6	0.7	0.7	0.8
15	0.7	0.8	0.9	1.0
20	0.8	0.9	1.0	1.3
25	0.9	1.0	1.1	1.5
30	1.0	1.1	1.3	1.7
35	1.1	1.2	1.4	1.9
40	1.2	1.3	1.5	2.1
45	1.3	1.4	1.6	2.3
50	1.4	1.6	1.8	2.6

DISCUSSION

Two other factors which will influence line broadening in the diffraction traces of real fibrous polymers are (1) preferred orientation, (2) crystallite size distribution. We have seen that the smaller crystallites tend to lie at larger angles of misorientation to the fibre axis[4]; in the presence of factor (1) this will lead to increased integral breadth, decreased apparent crystallite size and an increased K parameter. This point has been demonstrated in a subsidiary experiment on the structure of drawn poly(oxymethylene) rods which have a relatively highly crystalline structure with high preferred orientation. Unrotated specimens showed diffraction profiles yielding apparent crystallite sizes about 10% lower than values obtained with rotated specimens*. Indeed, the use of rotated specimens or finely cut and randomized fibre lengths[20] are well known techniques used to remove the effects of preferred orientation. In the present investigation preferred orientation was removed by rotation of the masks during the recording of the optical transforms.

The small discrepancies between the K parameters established by optical diffraction methods, and the K parameters determined from the ratio of lattice–fringe measurements to X-ray or electron diffraction estimates, must therefore be accounted for in terms of the effect of crystallite size distribution. It is not easy to construct masks to test the influence of size distribution, and our attempts at this have proved unsatisfactory. However, quantitative work is in hand to evaluate K parameters from intensity profiles computed from simulated size distributions. Preliminary results show that indeed a slight increase in K is caused by including a distribution of crystallite size rather than the mean size.

The most difficult practical exercise in fibre characterization by diffraction methods is the estimation of distortion. We see here that the profile-function parameter f decreases with increasing distortion; unfortunately, with real fibres we have only been able

Table 4 Values of K due to combined effects of size and distortion K_{SD} (Half width)

Distortion % Number of layer planes	0	4.0	8.0	10.0
10	0.5	0.6	0.6	0.7
15	0.6	0.7	0.8	0.9
20	0.7	0.8	0.9	1.1
25	0.8	0.9	1.0	1.2
30	0.9	1.0	1.1	1.3
35	1.0	1.1	1.2	1.5
40	1.1	1.2	1.3	1.7
45	1.2	1.3	1.5	1.9
50	1.3	1.5	1.7	2.1

Table 5 Comparison of true and apparent crystallite sizes from direct electron-microscope measurement and from diffraction analysis

	Specimen				
Technique	Carbon Fibre (Type 1)		PPT (PRD 49)	Carbon whisker	Carbon Fibre (Type A)
1 Lattice-fringe image (nm)	3.5a	4.5b	5.4	15.0	1.7
2 Electron diffraction (nm)	4.3c	5.2d	7.2	10.0	–
3 X-ray diffraction (nm)	3.8e	5.1f	6.7	–	1.5
K parameter 1/2	0.8	0.9	0.7	1.5	–
1/3	0.9	0.9	0.8	–	1.1
Number of lattice lines	11	14	14	45	6
Distortion %	3	3	1.5	0	>10
K_{SD} Parameter from *Table 3*	0.7	0.8	0.7	1.3	>1.0

a, mean value from dark-field image; b, mean value from bright-field image; c, all crystallites included; d, equatorial trace; e, rotated specimen; f, equatorial trace

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* A. M. Hindeleh and I. M. Ward, unpublished

to establish significant values of f in exceptional cases. The problem of determining f is made difficult by uncertainties in assessing the background parameters and the tails of closely overlapping peaks, thus in most cases the resolved profile-function parameter can give only a rough guide to the level of distortion present. There are, of course, several methods available for evaluating distortion when two or more orders of a reflection are present in the diffraction trace (see for example Buchanan and Miller[8]). A detailed study of these methods is in preparation; indications are that none are entirely satisfactory. Nevertheless, many workers in the field of fibrous polymers would like a simple method for estimating distortion, and that due to Hosemann[10] might be considered. The Hosemann relationship is $g=35/n$ where n is the number of orders of a particular reflection, and g is the disorder as a percentage. Thus, in terms of our perfect grating used for the instrument broadening correction, $n=17$ and g should be 2%. It seems unlikely that such a high degree of disorder exists in this lattice, indeed 1% would seem high. If we consider the most highly ordered fibre studied in this laboratory, the PRD 49 (PPT) fibre, 18 layer lines can be seen in the electron diffraction pattern. Again a disorder of 2% seems high; indeed we might expect the longitudinal distortion to be similar to the measured lateral distortion of 1.5%[18]. In terms of specific reflections, most fibrous polymers show one, two or three orders only, so that the best distortion to be expected should be 12%. If we consider our masks of 0, 4, 8, and 10% input distortion, with 9, 4, 3 and 2 orders visible in the optical transforms, then the Hosemann relationship indicates distortions of 4, 9, 12, and 17% respectively. Despite the probability that the graph plotter imparts some additional distortion, these latter values seem to be too high. We suggest that an expression of $g=20/n$ would be more realistic.

It must be pointed out that all intensity traces from the masks with input distortion supposedly of the first kind, showed increasing line broadening with increasing order of the reflection, hence revealing the so-called distortions of the second kind. In these experiments we have been unable to draw a grating without distortion, apparently of the second kind, and with real fibres have found only one example where this kind of distortion is absent. This example has a graphite whisker which gave six orders of 001 in the electron diffraction trace with no increased line broadening with increased order. No other fibrous material is so perfect and it is proposed that, in terms of the normal fibrous materials, to draw distinctions between kinds of distortion is unwarranted.

CONCLUSIONS

The Scherrer K parameter is a function of both crystallite size and lattice distortion. Empirical values of K for both integral breadth and half width have been obtained from optical transforms which simulate these effects. These parameters are in reasonable agreement with values obtained by finding the ratio of the direct size measurement obtained from lattice–fringe images and the apparent crystallite size from diffraction analysis.

The following procedure is suggested for the best estimate of true crystallite size from an X-ray diffraction trace:

(1) Resolve separate profiles by means of a peak resolution procedure such as the one reported here.
(2) Estimate the distortion from the profile-function parameter f or the empirical formula $g=20/n$.
(3) Calculate the mean apparent crystallite size using $K=1$ in the Scherrer formula.
(4) Determine the mean number of layer planes in the crystallites by dividing the mean apparent crystallite size by the lattice spacing.
(5) Use *Tables* 3 or 4 to obtain an estimate of the K parameter by which the apparent crystallite size must be multiplied to give the best estimate of true crystallite size.

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