INTERNATIONAL ATOMIC ENERGY AGENCY
UNITED NATIONS EDUCATIONAL, SCIENTIFIC AND CULTURAL ORGANIZATION

INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS
34100 TRIESTE (ITALY) - P.O.B. 586 - MIRAMARE - STRADA COSTIERA 11 - TELEPHONE: 2240-1
CABLE: CENTRATOM - TELEX 460392 - I

SMR/206- 15

"SCHOOL ON POLYMER PHYSICS"

27 April - 15 May 1987

"CRYSTALLINITY, CRYSTALLITE SIZE AND LATTICE DISTORTION IN POLYMERS"

Professor Abdelnour Michael HINDELEH
Department of Physics
University of Jordan
P.O. Box 13093
Amman, Jordan

Abstract

The uses and applications of two methods for the analysis of the X-Ray diffraction scans of polymers will be discussed.

As a prerequisite for the evaluation of Crystallinity and Crystallite Size, the overlapping peaks in the scan must be resolved using adequate crystallographic and mathematical procedures. The resolved peaks are fitted to a combined function (Gaussian / Cauchy), which appears to give the best estimate of crystallite size.

The evaluation of distortion in the crystal lattice, and the determination of the true crystallite size will be illustrated.

I. INTRODUCTION

It is generally accepted that estimates of structural parameters such as X-ray crystallinity, crystallite size, orientation, birefringence, and degree of polymerization in polymers may be related to the physical and chemical properties such as tensile strength, elongation, elastic modulus, yield point, abrasion resistance, degree of swelling, moisture content, and chemical reactivity. But unless the methods of measurement are on a sound basis, the relations between the different properties remain empirical.

Among the different methods used for the evaluation of crystallinity and crystallite size in polymers, I will suggest two methods for the analysis of the X-ray diffraction trace of polymers.

Method 1: Developed first by Wakelin et. al.(1) for the evaluation of Crystallinity in cotton, and applied for other polymers. A "Correlation Crystallinity Index" is determined.

Method 2: Developed by Hindeleh and Johnson(2) for the evaluation of Crystallinity and Crystallite Size in any polymer. A "Multipeak Resolution Crystallinity" is obtained, in addition to Crystallite Size.

II Method 1: The Correlation - Crystallinity Index

The basis of the method is the X-ray scattering law termed the "Law of Conservation of Intensity" by Vainshtein (3), which implies that when x-ray diffraction takes place, the total scatter in reciprocal space due to regions with lattice perfection and the total scatter due to an equivalent set of completely disordered atoms is exactly equal. Equivalent regions of the same material with intermediate states of lattice order will also have exactly equal total scatter in reciprocal space. The validity of this law in connection with fibrous polymers was thoroughly investigated[4] and it was found that the scattering by equal regions of ordered and disordered crystal lattices will vary by ~1%.

The method requires the preparation of two standard specimens representing the following states:

(i) The best-ordered lattice of the material under investigation, called maximum crystalline state (C_{max}), and it is assigned an index of 100.

b) The least-ordered lattice of the same material, called (C_{min}), and it is assigned an index 0.

Then for the evaluation of crystallinity, the specimen with unknown intermediate lattice order (C_{int}), will be ranked between C_{max} and C_{min}, and a "correlation crystallinity index (CCI) will be calculated according to the following procedure:

(a) The total scatter under each of the diffraction traces of C_{max}, C_{min} and C_{int} is normalized into a convenient area.

Figure 1 is a simulation of a set of traces of Viscose Rayon (Regenerated Cellulose II). The Figure illustrates clearly how the three curves, after normalization, oscillate around each other.

(b) The intensity differences $(C_{max} - C_{min})$ and $(C_{int} - C_{min})$ are then measured at small angular increments along a large angular range (say 5-60° 2θ), and plotted as illustrated in figure 2.

(c) The CORRELATION CRYSTALLINITY INDEX will then be:

$$CCI = \text{slope of } \frac{(C_{int} - C_{min})}{(C_{max} - C_{min})} \times 100 \quad \text{----} [1]$$

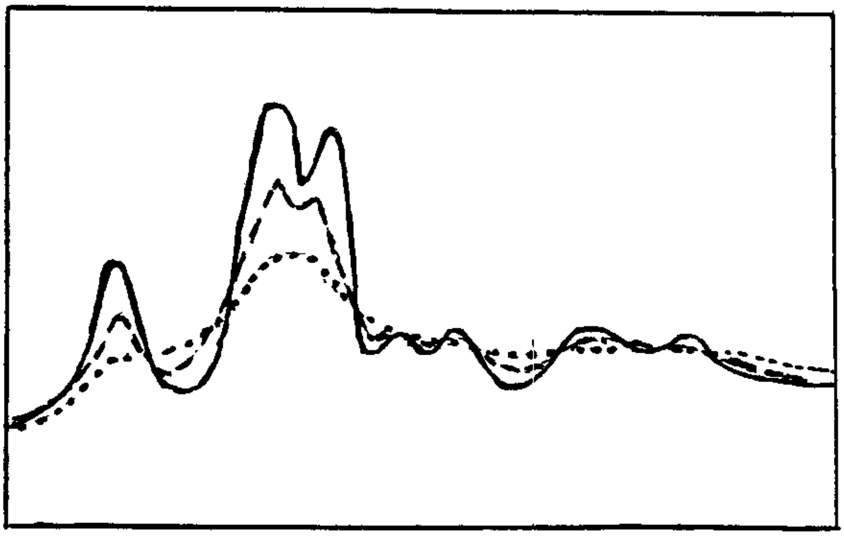


Fig.1: Simulation of the diffraction traces of C_{max} —— C_{min} .... and C_{int} ---- of Viscose Rayon (Regenerated Cellulose II)

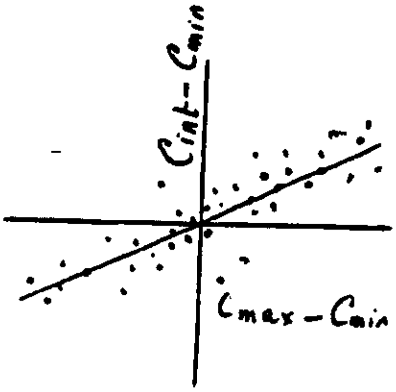


Fig. 2 Regression Line of $(C_{int} - C_{min})$ on $(C_{max} - C_{min})$

III. Method 2: Multipeak Resolution Crystallinity

X-Ray diffraction patterns from fibres generally contain a few closely overlapping peaks, each broadened by the contributions of crystallite size, crystallite-size distribution, and lattice distortion. In order to achieve complete characterization of a fibre by X-Ray diffraction methods, it is first necessary to separate the individual peaks, and then to separate the various profile-broadening contributions. Subsequently we can obtain measures of crystallite size, lattice distortion and peak-area crystallinity, to add to estimates of other characteristics obtained in complimentary experiments.

The Multipeak Resolution Crystallinity Method was developed by Hindeleh and Johnson(2) for the measurement of crystallinity and crystallite size in polymers, whether they are natural (like Cotton and Ramie) or synthetic (like Nylon, PET, Cellulose Triacetate, or Kevlar).
The method gives a better insight into the crystalline structure of the polymer, but requires rigorous mathematical analysis of the X-Ray diffraction trace, and computational facilities.

The equatorial X-Ray diffraction scan of a randomized polymer sample is usualy recorded in an X-Ray diffractometer, followed by the Computational analysis.

Four major computational steps are necessary to separate the individual peaks and the different profile broadening components :

A) Correction and Normalization of the diffraction data,

B) Resolution of the total peak scattering from the so-called background scattering,

C) Correction of the resolved profiles for instrumental broadening,

D) Separation of the corrected profiles into size and distortion broadening.

III A) Correction and Normalization of the X-Ray Diffraction Trace

a) The experimental intensity data (I_1) is corrected first for Polarization

$$I_2(2\theta) = I_1(2\theta)\cdot\left(2/(1+\cos^2 2\theta)\right) \quad \text{------} \quad [2]$$

b) I_2 is then corrected for the Lorentz geometric factor to give

$$I_3(2\theta) = I_2(2\theta)\,\sin 2\theta \qquad \text{for powder specimens}$$

$$I_3(2\theta) = I_2(2\theta)\;2\sin^2\theta\cos\theta \qquad \text{for fibre bundle with cylindrical symmetry} \quad [3]$$

c) Normalization of the intensity scans, (when comparing a set of samples), using a procedure based on Vainstein's law of conservation of intensity. This law states that total scatter over identical regions of reciprocal space will be equal despite different degrees of lattice order.

$$I_4(2\theta) = I_3(2\theta) \times \frac{AR2}{AR1} \quad \text{---------} \quad [4]$$

where $AR1$ is the area under the corrected scan, and $AR2$ is the normalized area.

d) $I_4(2\theta)$ consists of contributions from the Atomic scattering factor(f^2) and the Compton incoherent scatter C. $I_4(2\theta)$ is corrected for the removal of incoherent scatter as follows:

$$I_5(2\theta) = I_4(2\theta)\frac{\overline{f}(2\theta)}{\left[\overline{f}(2\theta)+\overline{C}(2\theta)\right]} \quad \text{- - - - - - - -} \; [5]$$

where $\overline{f}^2 = \left(\Sigma N_i f_i^2\right) / \Sigma N_i$, and - - - - - - [6]

$\overline{C} = \left(\Sigma N_i C_i\right) / \Sigma N_i$ - - - - - - - - - - - - [7]

where N_i is the number of atoms of type i in the molecular repeat, and

C_i is the incoherent scatter for atoms of type i.

A correction for air scatter may be carried out. A correction for absorption within the specimen is negligible over the range of 2θ normally covered, and so will be neglected here.

The corrected data are then held in a computer file for subsequent profile resolution.

III·B) Resolution of the Overlapping Peaks

The corrected intensity data (or corrected diffraction trace), are then resolved into peaks and background scatter. Before talking about Resolution it is important to make the following explanations:

(1) An intensity peak has a profile f, an amplitude A, a width at 50% amplitude W, and a position $P(2\theta^\circ)$ on the diffraction trace, which relates the Intensity and $2\theta^\circ$ within a defined $2\theta^\circ$ range (say $10 - 50^\circ 2\theta$).

ii) For a Gaussian profile $f = 1$, for a Cauchy profile $f = 0$, and for a combined Gaussian/Cauchy profile, which has been found to apply to polymers, f ranges between -0.5 and 1. As f becomes < 1 the tails of the profile increase as shown in Figure 3.

iii) So each peak profile in the diffraction trace is considered to have the form:

$$I_S(2\theta) = f_t\, G_t + (1 - f_t)\, C_t \quad \text{-------------} \quad [8]$$

where G_t is the Gaussian function

$$G_t = A_t \exp\left\{ -\ln 2 \left[\frac{2(X - P_t)}{W_t} \right]^2 \right\} \quad \text{------} \quad [9]$$

and C_t is the Cauchy function

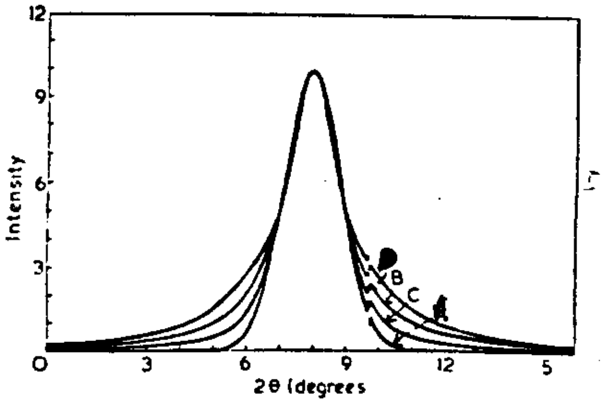
$$C_t = A_t \Big/ \left\{ 1 + \left[2\,(X - P_t)/W_t \right]^2 \right\} \quad \text{-----} \quad [10]$$

where $t = 1, 2, 3 \text{-----} B$; where B is the number of peaks to be resolved,
and X is the 2θ value at which the intensity is calculated.

iv) The scatter from disordered molecules in the polymer is considered to have the polynomial form

$$R = a + bX + cX^2 + dX^3$$

and corresponds to the so-called background scatter.



A) Gaussian $f = 1$
B) Cauchy $f = 0$
C) Combined Gaussian/Cauchy $f = 0.5$
D) Combined Gaussian/Cauchy $f = -0.5$

Figure 3.

The Multipeak Resolution Program requires the assignment of initial approximate values of f, A, W and P for each crystallographic peak to be resolved, and zero values for the parameters a, b, c and d of the background.

The function to be minimized to find the best-fit parameters of the resolved peaks and background is:

$$S = \sum_{i=1}^{n} \left[I_{(calc)_i} - I_{(norm)_i} \right]^2 \quad \text{..........} \quad [11]$$

$$\text{where } I_{(calc)_i} = \sum_{t=1}^{B} \left[f_t G_t + (1-f_t) c_t \right]_i + R_i \quad \text{------} \quad [12]$$

Here n is an array of data points of Intensity I versus the 2θ angle.

The output is in the form of a list of optimum parameters, the coordinates and area of each resolved peak, the coordinates and area of the background, and the areas under the resolved peaks relative to the area under the unresolved scan.

Several optimization (minimizations) procedures have been tried. The minimization procedure due to POWELL (called Powell 64)(5) was found satisfactory, and was incorporated in the Resolution program(2). It employs the method of conjugate directions and ensures efficient convergence of the function S. Although no bounds are needed to be put on the parameters, it is possible in this procedure to constrain any of the parameters during any optimization cycle by appropriate ordering of the parameter list.

Figures 4-13 show some of the applications of this method to a number of natural and man-made polymers. CRYSTALLINITY is then calculated as follows:

$$\% \text{ Crystallinity} = \frac{\text{Area under the Resolved Peaks}}{\text{Total area under the scan}} \times 100 \text{ ——— } [13]$$

According to the classical two-phase theory of structure, natural and man-made polymers consist simply of crystalline and non-crystalline (amorphous) regions. Accordingly, the area under the resolved peaks would essentially be a contribution from the crystalline part of the polymer, while the area under the background would essentially be a contribution from the amorphous part of the polymer. It is now more usual to discuss crystallanity in terms of PARACRYSTALLINITY (7) in which lattice distortions contribute to the background scatter, which was assumed to be mainly a contribution from the amorphous component.

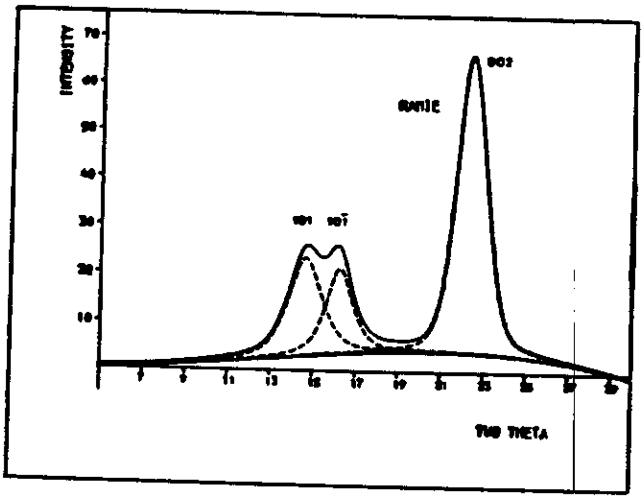


Fig. 4 Ramie (Cellulose I)

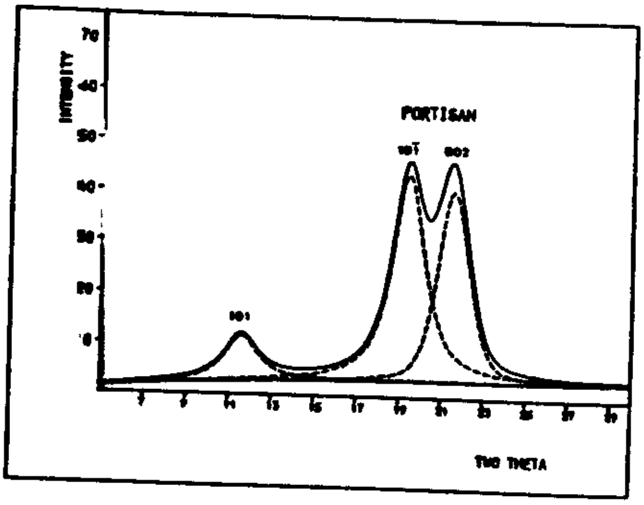


Fig. 5 Fortisan (Cellulose II)

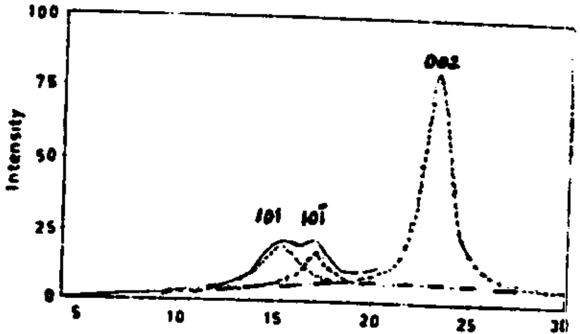


FIG. 6 Typical example of the x-ray diffraction trace of cotton (Menoufi) resolved into three peaks (101, 10$\bar{1}$, and 002) and a background.

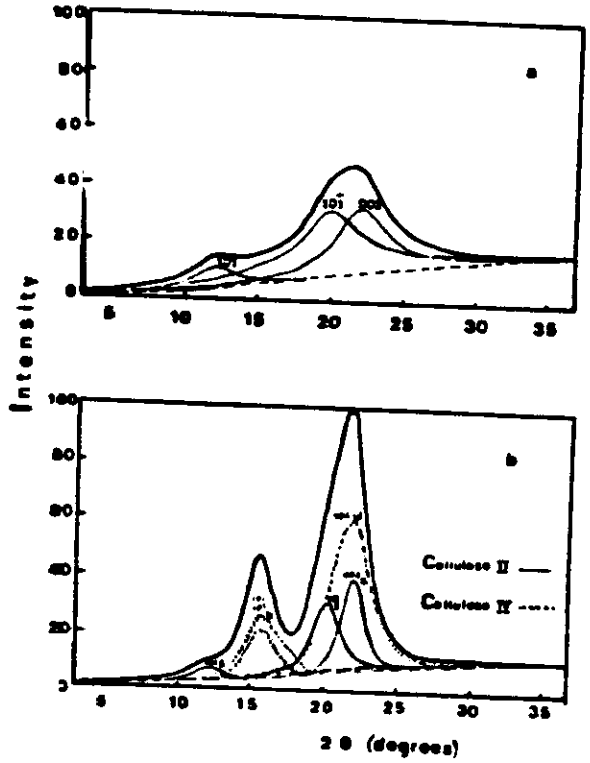


FIG. 7 X-ray diffraction traces of viscose rayon resolved into peaks and background: (a) annealed rayon at 120°C in nitrogen gas resolved into three peaks related to cellulose II and background scatter; (b) annealed rayon at 270°C in glycerol resolved into a background and six peaks: three peaks related to cellulose II and three peaks related to cellulose IV.

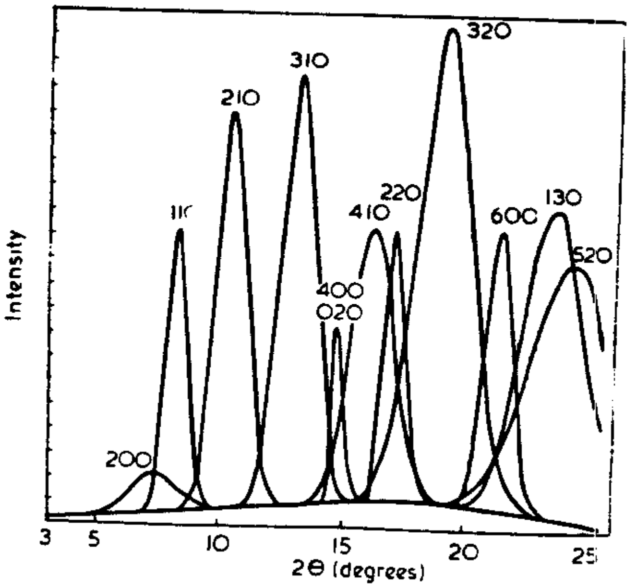


Figure 8 Corrected trace of *Figure* 2 resolved into eleven Gaussian peaks and a polynomial background

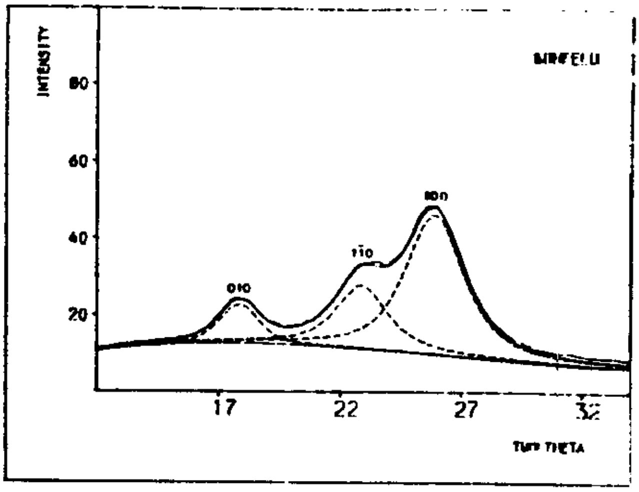


Fig. 9 Polyethylene Terephthalate

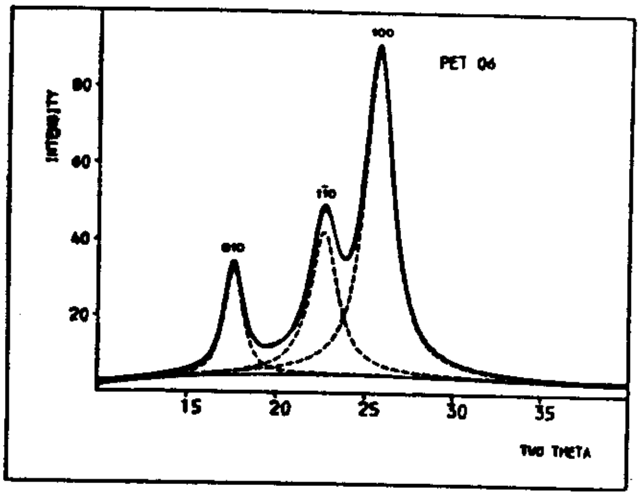


Fig. 10 Polyethylene terephthalate

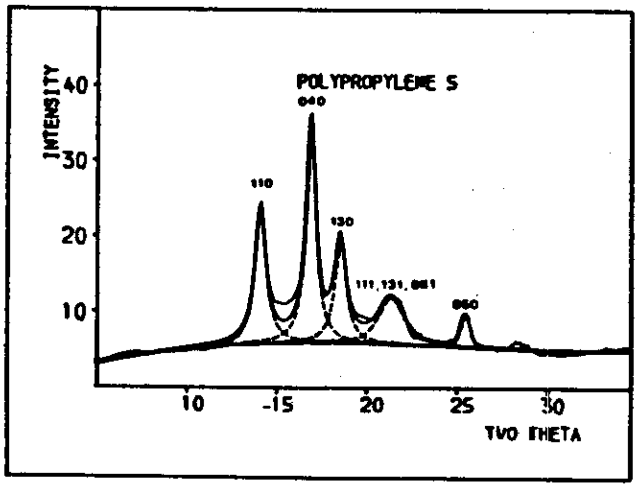


Fig. 11 Polypropylene

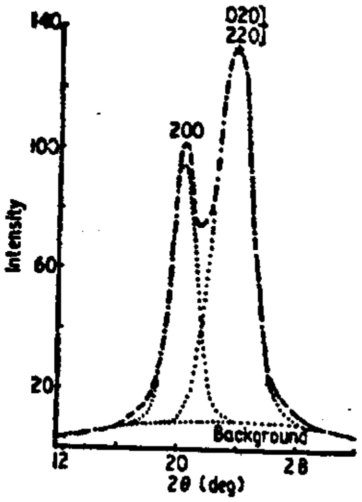


Fig. 12 Nylon 6

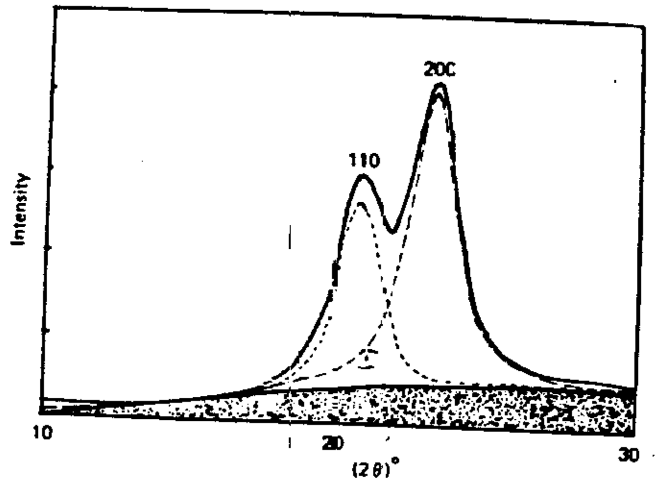


FIG. 13. The equatorial intensity of the wide-angle x-ray diffraction pattern of Kevlar 29, resolved into two peaks and a background.

Examples on the application of the Multipeak Resolution Program to fields other than X-Ray Diffraction:(2)

(i) Ion Exchange Chromatography

An amino-acid analysis of hair from normal children includes peaks from isoleucine, leucine, and norleucine, whereas the analysis of hair from children suffering from homocystinuria suggests the presence of a small overlapping peak due to a mixed disulphide of homocysteine and Cysteine (figure 14). The Resolution program successfully resolved the data from abnormal hair into four peaks including the peak due to the mixed disulphide (Peak B, figure 12). With data from normal hair, the height and width parameters for an assumed peak related to the mixed disulphide rapidly became negligible after resolution, thus proving its absence from the spectrum. The percentage of the mixed disulphide could be calculated from the area under the relevant peak.

(ii) Infrared Spectroscopy

The infrared spectrum for an undrawn nylon tape is given in figure 15. After trials based on 6 and 7 peaks, the spectrum was finally resolved into 8 Gaussian peaks as shown in Figure 15.

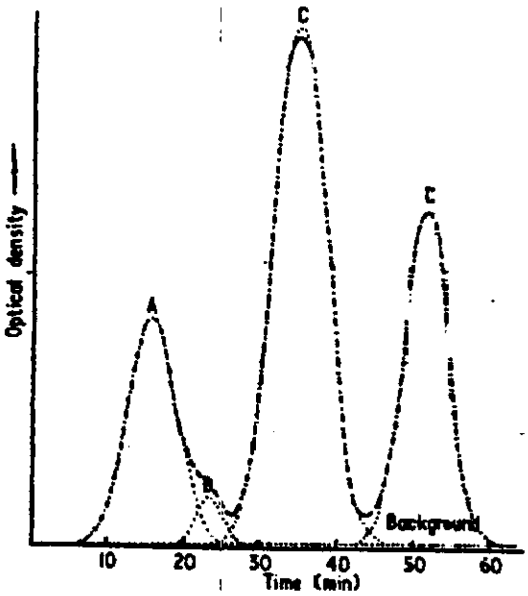


Figure 14 Part of trace from spectroscopic output of amino-acid analysis of diseased hair, dashed, resolved into four Gaussian peaks: A, isoleucine; B, mixed disulphide of homocysteine and cysteine; C, leucine; D, norleucine; dotted, and a straight-line background.

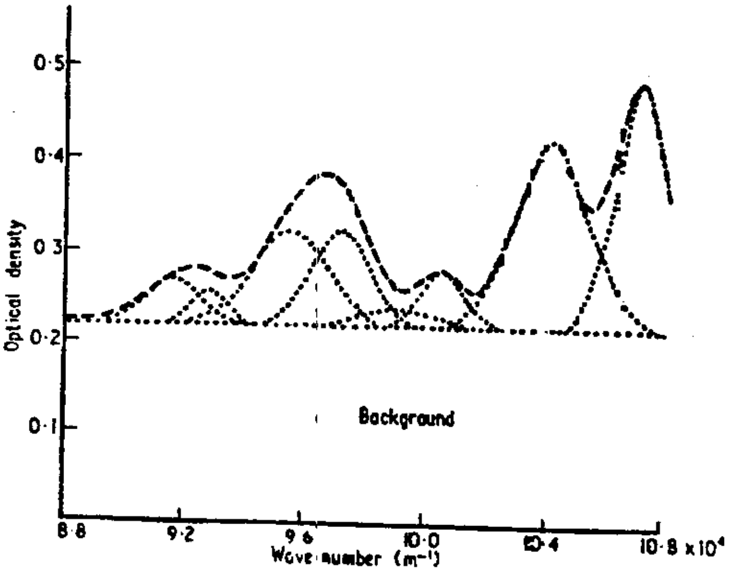


Figure 15 Part of infrared spectrum of undrawn nylon 6 tape, dashed, resolved into eight Gaussian peaks, dotted, and a straight-line background. The optical density is in arbitrary units.

III C) Instrumental Broadening Correction in X-Ray Diffraction

The two most common methods used to correct the resolved peak profiles for the broadening imposed by the finite width of the X-Ray beam in the diffractometer, are due to Jones(6) and Stokes(7). Both are essentially unfolding or deconvolution methods, but the Jones method defines specific functions for both the uncorrected and the instrumental broadening profile. If the resolved peak has a Gaussian profile, then

$$\beta^2 = B^2 - b^2 \quad \text{.........} \quad [14]$$

where B is the integral breadth of the resolved peak, b is the instrumental breadth, and β is the corrected breadth. Here b is considered to be the integral breadth of the main diffraction peak of hexamethylene tetramine crystals compacted at 85°C(2); b is used as a standard for instrumental broadening peak.

If the resolved peak is Cauchy, then

$$\beta = B - b \quad \text{.........} \quad [15]$$

Considering the resolved peak to have a combined Gaussian/Cauchy function, then

$$\beta = f\,(B^2 - b^2)^{\frac{1}{2}} + \left[(1-f)\,(B-b)\right] \quad \text{.........} \quad [16]$$

The Stokes method is essentially a Fourier transform method making use of the entire profiles from the resolved peak of the polymer, and the hexamethylene tetramine main diffraction peak.

It is a reasonably straightforward computation.

A comparison between the crystallite sizes after applying both types of correction on the most crystalline samples of Cellulose (Ramie and Fortisan) showed that the Jones corrections were within 3% of the Stokes corrections, when equation 16 was used. However, the current procedure is to apply Stokes deconvolution procedure for all resolved peaks.

Figure 16 illustrates a deconvolution operation. It shows a profile before deconvolution, an instrumental broadening profile, and the deconvoluted (net) profile.

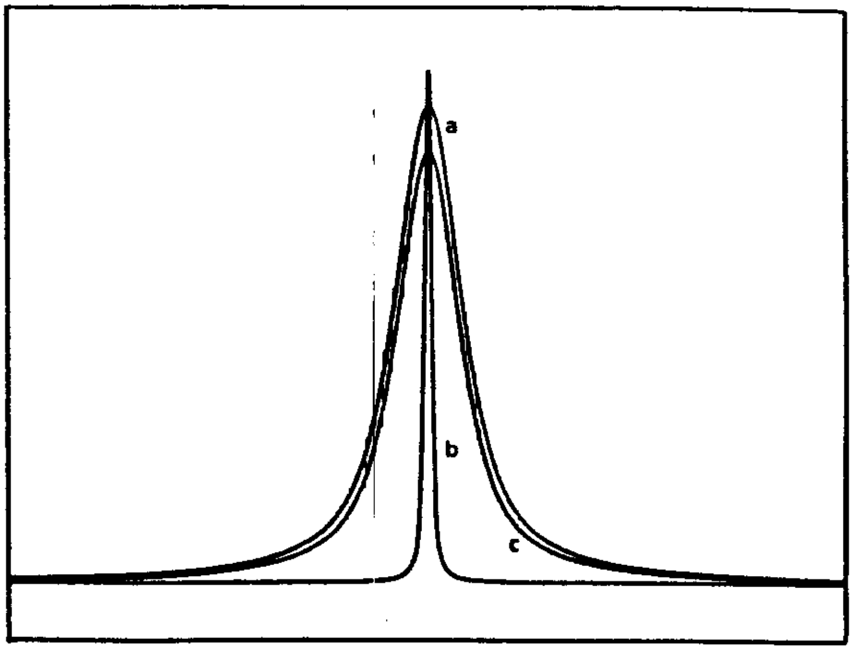


Figure 16. Deconvolution correction for instrumental broadening Profile b unfolded from Profile a to give Profile c.

III D) Calculation of the Apparent Crystallite Size ($\bar{L}_{hkl}$), The Lattice - Distortion Parameter (g), and The True Crystallite Size ($\bar{D}_{hkl}$)

(1) The Apparent Crystallite Size normal to the hkl netplanes is calculated according to Scherrer's equation

$$\bar{L}_{hkl} = \frac{K\lambda}{\cos\theta \; d(2\theta)} \quad \text{............} \quad [17]$$

where K is a constant ≈ 1, λ is the wavelength of the X-ray, and $d(2\theta)$ is the corrected integral breadth β expressed in Radians. The unit of $\bar{L}$ and λ is nm. θ is the Bragg angle.

(2) Calculation of the Lattice Distortion and the True Crystallite Size

There are several methods for separating the size and distortion broadening of the resolved and corrected peak profiles. Many of these methods have been discussed at length by Buchanan and Miller(8); however, they were unable to state which method gave the most realistic evaluations. The methods had been tested by comparison with electron-microscope measurements by Hindeleh, Johnson and Montague(9). It was concluded that Hosemann's method gave the best estimate of lattice distortion.

In all cases at least 3 orders of an X-Ray reflection are required to find out an appropriate relation between the integral breadth δb, where $\delta b = \frac{1}{L}$ and has the unit nm^{-1}, and the order of reflection.

According to Hosemann's theory of Paracrystallinity (10) the lattice-distortion parameter (g) is defined as the statistical fluctuation of netplane distance $\bar{d}$:

$$g = \left[\overline{d^2} / (\bar{d})^2 - 1 \right]^{1/2} \quad \text{.......... [18]}$$

The presence of this distortion (g) shows an increase in the integral breadth δb proportional to the square of the order of reflection (l). Moreover, with a growing lattice the statistical fluctuations finally become so large that the construction is halted as shown at the arrow in Figure 17 (11).

$$\delta b = \frac{1}{L} = \left[\frac{1}{\bar{D}} + \left(\frac{\pi^2 g^2}{\bar{d}} \right) l^2 \right] \quad \text{....... [19]}$$

where $\bar{L}$ is the apparent crystallite size,
$\bar{D}$ is the true crystallite size.

Hence the average Netplane Layers will be

$$\bar{N} = \frac{\bar{D}}{\bar{d}} \quad \text{.......... [20]}$$

Figure 18 illustrates 3 orders of reflection of a paracrystalline material with $g = 5\%$(9). If δb versus ℓ^2 are plotted, a straight line curve will be obtained. The intercept of the curve with the ordinate gives the reciprocal of $\bar{D}$. From the slope of the curve, the lattice distortion parameter g is calculated.(10)

Figure 19 shows δb versus ℓ^2 for PRD49 with $\bar{D}_{002} = 38\,\mathrm{nm}$ and $g = 2.0\%$(11). Figure 20 shows δb versus ℓ^2 for Kevlar 29 with $\bar{D}_{002} = 14.9\,\mathrm{nm}$ and $g = 4.6\%$(12). Figure 21 shows δb versus ℓ^2 for an electron diffraction pattern from the skin region of carbon fibre with $\bar{D}_{001} = 3.5\,\mathrm{nm}$ and $g = 2.0\%$; the Figure shows also δb versus ℓ^2 for the 001 electron diffraction profiles of a carbon whisker, an exceptionally perfect graphite material with $\bar{D}_{001} = 10.0\,\mathrm{nm}$ and $g =$ ZERO. This represents the only case where no distortion was found in a fibrous specimen(9,13).

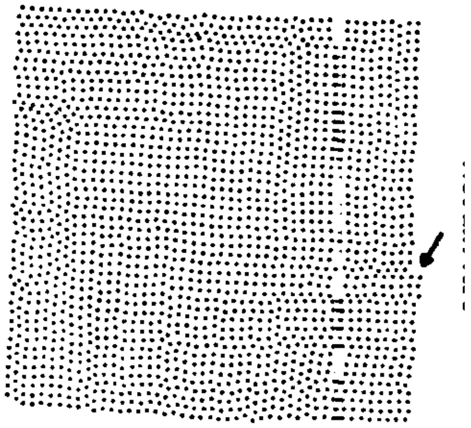


Fig. 17

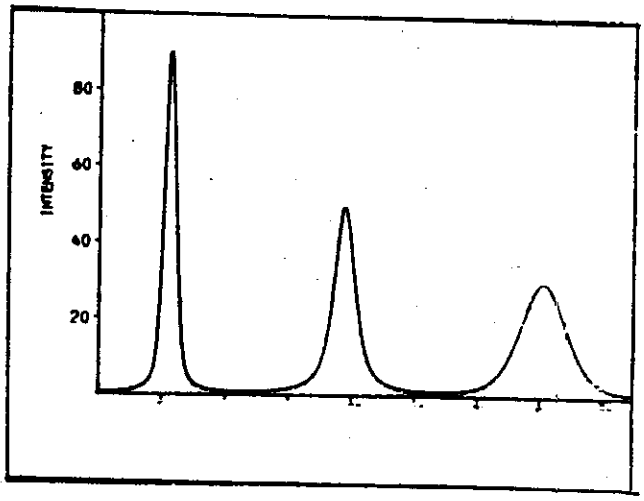


Fig. 18

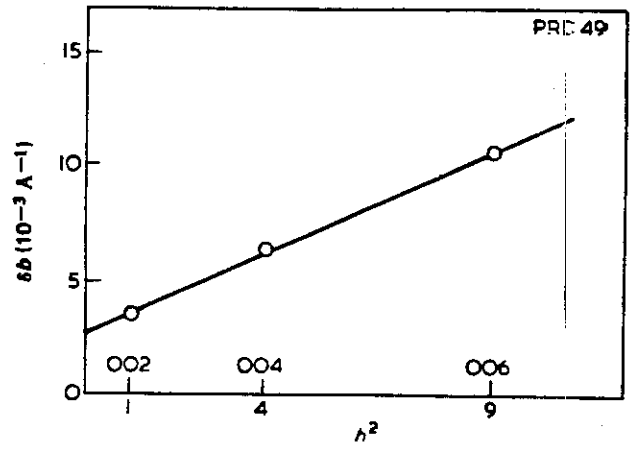


Fig. 19

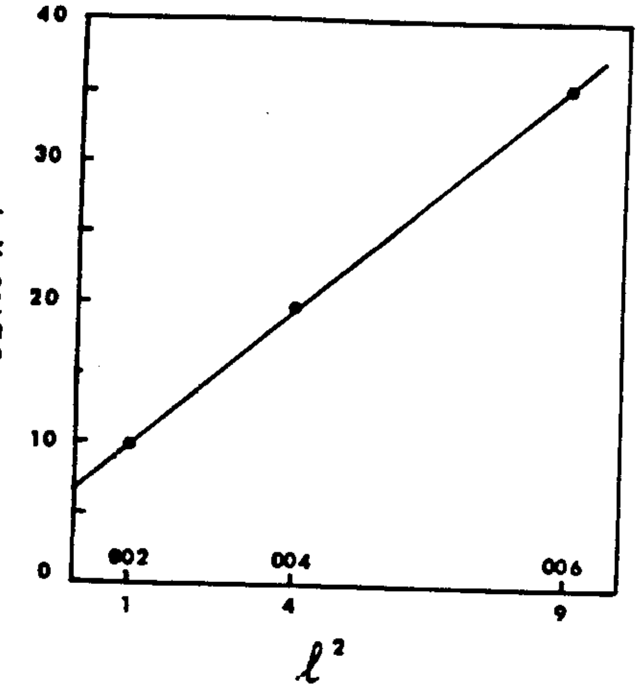


Fig. 20

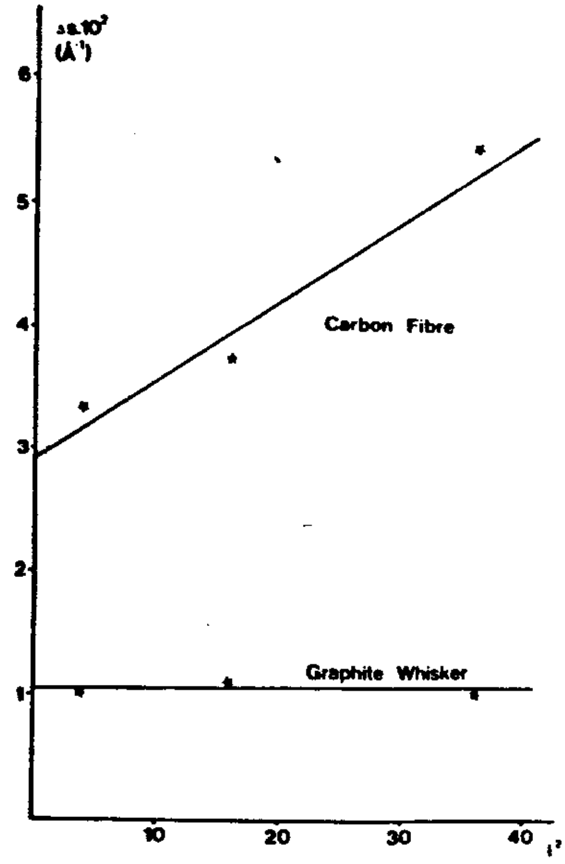


Fig. 21

CONCUSION

1. The "Correlation Crystallinity Index" method is an easy and useful method for routine comparison of changes in the crystalline state of a series of samples, on condition that C_{max} and C_{min} samples could be prepared. However, this method does not allow an evaluation of crystallite size.

2. The "Multipeak – Resolution Crystallinity" method can give an evaluation of the Crystallinity and crystallite size, followed by analysis of distortion and true crystallite size determination when three or more orders of a reflection are present in the Diffraction pattern.

3. It is not sufficient to have a good mathematical resolution alone; all peaks must be significant in crystallographic or structural terms.

4. The combined function (Gaussian/Cauchy) appears to give the best estimate of crystallite size.

5. Hosemann's method appears to give the best estimate of the lattice distortion(g) and true crystallite size. Apart from graphite which showed $g - 0$, Crystallites with distortions may be termed "Microparacrystallites", as proposed by Hosemann.

REFERENCES

1 1. J.H. Wakelin, H.S. Virgin, and E. Crystal, J. Appl. Phys., 30, 1654(1959).

2. A.M. Hindeleh and D.J. Johnson

a) J. Phys. D: Appl. Phys. 4, 259 (1971)

(b) Polymer 13, 27 (1972); 13, 423 (1972); 15, 697 (1974); 19, 27 (1978)

A.M. Hindeleh, Text. Res. J. (U.S.A.), 50, 10, 581 (1980); 50, 11, 667 (1980).

3. B.K. Vainshtein, "Diffraction of X-Rays by Chain Molecules", Elsevier Publishing Co., London, 1966, p. 178

4. A.M. Hindeleh and D.J. Johnson, Polymer, 11, 666 (1970)

5. M.J.D. Powell, Comput. J., 7, 155 (1964)

6. F.W. Jones, Proc. Roy. Soc., A116, 16 (1938)

7. A.R. Stokes, Proc. Phy. Soc., A61, 382 (1948)

8. D.R. Buchanan and R.L. Miller, J. Appl. Phys., 37, 4003 (1966)

9. A.M. Hindeleh, D.J. Johnson and P.E. Montague "Computational Methods for Profile Resolution and Crystallite Size Evaluation in Fibrous Polymers", in "Fiber Diffraction Methods", ACS Symposium Ser. No. 141, 1980, pp. 149-182

10. R. Hosemann and W. Wilke, Makromol Chem. 118, 230 (1968).

11. A.M. Hindeleh and R. Hasemann, Polymer, Pol. Comm., 23, 1101 (1982)

12) A.M. Hindeleh, N.A. Halim and K. Ziq, Macromol Sci.: Phys., B23(3), 289 (1984)

13) S.C. Benett and D.J. Johnson, Carbon, 17, 25 (1979)