INTRODUCTION

Mechanical, as well as physical and chemical properties of fibrous polymers depend upon the super- and supra-molecular organization of atoms, i.e., the nature and dimensions of the macromolecular structures. In the present decade, it would be possible to develop a "polymer metallurgy" for modifying the properties of polymers in a controlled manner by means of chemical treatments such as swelling, hydrolysis, grafting and cross-linking; physical treatments such as heating and stretching; and also by means of "alloying" additions of low molecular weight compounds. To achieve this end, a systematic knowledge is required about the crystallization behaviour of polymers - a multi-stage process wherein the macromolecules interact to form large and complex structures. If a precedence is drawn from the numerous X-ray diffraction line-profile studies of the internal structure of metals and alloys, it would follow that such studies may be of great significance in the elucidation of macromolecular order in fibrous polymers (or, polymers in general).

Systematic detailed X-ray studies on the structure of fibrous polymers are not as numerous as in the case of metals and alloys. This can be attributed to various difficulties which are encountered in analyzing the X-ray diffraction
patterns of fibrous polymers and to the lack of a unified theoretical approach which would satisfactorily account for the observed features of these patterns.

Recent studies have shown that polymers have a tendency to crystallize into an imperfect lattice with molecular chains assuming either an extended- or a folded-configuration. The unit cells in the lattices of fibrous polymers tend to deviate from their ideal positions on account of thermal vibrations of atoms, statistical disorder or dislocations of chains. Hosemann\(^3,4\) has suggested the name "paracrystal" for these particular lattices.

After proposing the theory of an "ideal paracrystal"\(^3,4\) in 1950, most of Hosemann's efforts were concentrated on explaining the anisotropy and diffuseness of small- and wide-angle X-ray diffraction patterns and verifying the important features of his theory by means of two-dimensional optical diffraction patterns of various lattice models\(^5,6,7\). It was not until 1963 that Bonart, Hosemann and McCullough\(^8\) proposed a method of separating the effects of thermal distortions (Type I), paracrystalline distortions (Type II) and small crystallite size through a quantitative analysis of the integral breadths of the line-profiles of various orders of reflection from a set of planes. They showed that the integral line breadth of a \(k^{th}\) order reflection from a small paracrystal is given by:

\[
\beta_{oko}
\]
where, $b$ is the average spacing of the reflecting (oko) planes, $g$ is the coefficient of variation of this spacing, and $L$ is the "weight-average" dimension of the paracrystallite along the normal to the reflecting planes. Since then, there have been very few applications of these results to fibrous polymers$^{9,10}$.

Tournarie$^{11}$ has criticized the use of integral breadth as a parameter of line breadth on the ground that it makes use of intensities measured at only a few points on the diffraction line-profile, and has recommended the use of variance—a concept which has been developed recently by Wilson$^{12,13}$.

**SUMMARY**

The present dissertation is mainly concerned with the development of a general theory of line-profile analysis which would satisfactorily explain the various measures of dispersion (i.e., integral breadth, variance, fourth-moment and Fourier coefficients) in terms of the effects of finite crystal size and paracrystalline distortions.

Theoretical calculations in terms of the ideal paracrystalline model show that the autocovariance function $J(t)$ of the distorted lattice, which is the mean value of the product $FF^*$ of the structure factors of a pair of unit cells separated by $m = t/b$ interplanar spacings, is given by:

\[
\beta_{oko}^2 = \frac{1}{L^2} + \frac{4g^4k^4}{b^2}
\]
\[ J(t) = \exp(-\alpha |t|) \quad (VI.2) \]

where, \( \alpha = \frac{2\pi b^2 k^2}{b} \).

The normalized distortion profile \( I_D(s) \), which is the Fourier transform of \( J(t) \), is Cauchy in shape:

\[ I_D(s) = \frac{2\alpha}{\alpha^2 + 4\pi^2 s^2} \quad (VI.3) \]

This theoretical result is thus in agreement with various experimental observations\(^1,14\) according to which polymeric X-ray diffraction profiles have a Cauchy shape.

The various measures of line-broadening can thus be expressed in terms of paracrystalline distortions as:

(a) Integral breadth

\[
\beta_D = \frac{\int_{-\infty}^{\infty} I_D(s) ds}{I_D(0)} = \frac{\alpha}{2} \quad (VI.4)
\]

(b) Variance-range function

\[
W_D = \frac{\int_{-\sigma_1}^{\sigma_2} s^2 I_D(s) ds}{\int_{\sigma_1}^{\sigma_2} I_D(s) ds} = \frac{\alpha (\sigma_1 + \sigma_2)}{2\pi^2} - \frac{\alpha^2}{4\pi^2} \quad (VI.5)
\]

where, \( \sigma_1 \) and \( \sigma_2 \) are the limits of \( s \) between which the profile is truncated and are usually large.
(c) Moment-range function

\[ \mu_D = \frac{\alpha (\sigma_1^3 + \sigma_2^3)}{2\pi^2} - \frac{\alpha^3 (\sigma_1 + \sigma_2)}{8\pi} + \frac{\alpha^4}{16\pi} \]  \hspace{1cm} \text{(VI.6)}

(d) Fourier coefficient

\[ \frac{J(t)}{J(0)} = \text{Fourier transform of } I_D(s) = \exp(-\alpha |t|) \]  \hspace{1cm} \text{(VI.7)}

The corresponding expressions for crystallite size broadening are already available\textsuperscript{12,15} and therefore the interpretation of these parameters becomes easy even if the crystallite size and paracrystalline distortion effects are simultaneously present.

In the present work, suitable developments have been made in the technique of obtaining the profiles of meridional X-ray reflections from fibrous polymers. A reflection method has been devised for obtaining the meridional oko profiles from tilted fibre cross-sections wherein the intensity of diffraction can be considerably increased while the broadening effect due to beam penetration is eliminated.

An improved methodology has been developed in this work for the analysis of polymeric X-ray diffraction profiles which helps to overcome the difficulties encountered in such an analysis. The optimization of the diffuse background under the discrete X-ray reflections is carried out by employing a modification of the Langford-Wilson technique\textsuperscript{16} of obtain-
ing the variance-range functions. Methods are also presented for obtaining maximum information from unresolved X-ray profiles (i.e., the overlapping peaks).

Indirect evidence, collected from various experimental results already available in literature, is presented to show the existence of paracrystallinity in cellulose. The probable reasons for the occurrence of Type II distortions in the cellulose lattice are also outlined.

CONCLUSIONS

The main conclusions which can be derived from the present study are as follows:

- The general theory of line-profile analysis developed here can successfully explain the various measures of X-ray diffraction line broadening.

- The variance-range method has great potential in the analysis of polymeric X-ray diffraction profiles. It offers special advantages over the integral breadth methods.

- The integral breadths obtained by Stokes' deconvolution method can be accurately predicted by the Wagner-Aqua equation \(^{17}\).

- The results obtained from four different methods of line-profile analysis are consistent among themselves.

- The axial lattice structure of ramie and jute (Cellulose I) and Tufcel (Cellulose II) are "paracrystalline".
Axial disorder is greater in "Tufcel" than in ramie, with jute occupying the intermediate position.

On account of the presence of Type II distortions, the lattice symmetry is lost in Cellulose I, giving rise to the observed odd-order 0k0 reflections. The average crystallite lengths in "Tufcel", jute and ramie are 150 Å, 260 Å and 430 Å respectively.

There is an inverse correlation between the g-value and the square-root of average particle size.

The results of the present study are expected to have a significant bearing on the analysis of imperfect substances other than fibres which have a paracrystalline structure. The routine analyses of polymeric XRD profiles can indeed be very rapid and reliable with the help of the proposed methodology.
REFERENCES