Chapter 1

Fibre Diffraction and Whole Powder Pattern Fitting in Polymers

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ABSTRACT

Crystal structure determination using a single crystal of any material has become a routine exercise. However in the case of fibres, the micro-crystallites are randomly arranged with their axis parallel to the fibre axis giving rise to poor reflections which are due to diffuse scattering, crystal structure determination is not possible. Hence crystal structure determination using poor fibre diffraction data is a challenging one. Model based correlations of X-ray diffraction data from fibrous materials are extensively discussed in a book by Fraser and MacRue (1973). The crux of the problem in fibre diffraction analysis is that the number of X-ray diffraction data is less than what could have been obtained for a single crystal. This aspect has limited the use of existing well developed crystallographic method such as Fourier synthesis of electron density or least squares refinement of atomic parameters.

INTRODUCTION

Crystal structure determination using a single crystal of any material has become a routine exercise. However in the case of fibres, the micro-crystallites are randomly arranged with their axis parallel to the fibre axis giving rise to poor reflections which are due to diffuse scattering, crystal structure determination is not possible. Hence crystal structure determination using poor fibre diffraction data is a challenging one. Model based correlations of X-ray diffraction data from fibrous materials are extensively discussed in a book by Fraser and MacRue (1973). The crux of the problem in fibre diffraction analysis is that the number of X-ray diffraction data is less than what could have been obtained for a single crystal. This aspect has limited the use of existing well developed crystallographic method such as Fourier synthesis.
of electron density or least squares refinement of atomic parameters. To get over this difficulty, Arnott and Wonacott (1966), Smith and Arnott (1978) have developed a method wherein the approach involves to incorporate the knowledge of chemical sequence like bond lengths and bond angles in molecular models and then by systematic trial and error, to adjust their conformations and positions in a unit cell to obtain a good agreement between observed and calculated amplitudes from the model parameters. This technique has been used to solve the crystal structure of collagen (Okuyama (2008)), silk-I (Okuyama et al) and silk-II modifications (Sangappa (2005)) and cotton fibres (Samir & Somashekar (2007)) and also of polymer (Hall & Somashekar 1991). We apologize, in advance, for the omission of some structures to which our survey could not reach.

In addition to the problem mentioned above, the parallelism of the crystallites is invariably imperfect and the diffracted intensities are distributed not in spot but along arcs the length of which increases with distance from the pattern center. This dissipation of diffracted intensity over increasing lengths of arc implies a similar rise in the threshold for observation and even at moderate distances from the pattern center all but the strongest intensities are merged in the background. This leads to the fact that the resolving power of the data is low since it is the diffraction furthest from center that defines the finer periodicities in crystals. In the following we describe a method for refining the positional and conformational parameters of model systems while retaining given stereo chemical constraints. It is readily adaptable for automatic digital computers and is related to one studied for DNA fibres and to others described for single crystals.

Mathematical Analysis of the Refinement Method

Essence of mathematics that goes into the methodology of refinement are reproduced from the earlier work of Arnott & Wonacott (1966). The 'best fit' considered to be that which minimizes.

\[
\sum_{i=1}^{M} \left( F_{o} - F_{m} \right)^{2} = \sum_{i=1}^{M} \hat{E}_{m}^{*} F_{m}^{2}
\]

(1)

where there are M observed diffraction amplitudes, Fo, and Fm are the corresponding amplitudes calculated for the model.

\[
F_{m} = \left( A_{m}^{2} + B_{m}^{2} \right)^{\frac{1}{2}} \frac{1}{K} \exp \left( -B \hat{A}^{2} / 4 \right)
\]

(2)

Where

\[
A_{m} = \sum_{p} f_{p} \left( h_{m} k_{m} l_{m} \right) \cos 2\pi \left( h_{m} x_{p} + k_{m} y_{p} + l_{m} z_{p} \right)
\]

(3)

and
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