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Research Note

An X-Ray Method to Analyse the Elastic Nature of Fibrous Materials — Azimuthal Scan of Diatropic Powder Diffraction Data for Cellulosic Fibres

SUMMARY

It is well-known that fibrous polymers are made up of crystallites stacked along the fibre axis and that changes in the stacking configuration can be brought about by chemical treatments. This paper oulines a method for studying the nature of stacking by making an azimuthal scan of a diatropic X-ray diffraction pattern. It is shown that it may be possible to use this approach to predict the elastic properties of fibrous polymers.

INTRODUCTION

In natural and synthetic polymers fibres behave as a polycrystalline aggregate consisting of small crystalline regions bound and separated by amorphous regions.

In natural cotton, the bulk of the fibre consists of cellulose crystallites which appear to follow a longitudinal helical course around the fibre axis with frequent reversals in direction. The chains of the helix make an acute angle with the fibre axis and this angle is generally referred to as the spiral angle. This underlying spirality is one of the factors determining the elastic properties of the fibre. The helix frequently changes direction so the cellulose crystallites are stacked

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along the axis of the fibre in the form of both right-handed and left-handed helices. The elastic behaviour of the fibre is partly due to this arrangement of crystallites within the fibre.

When a fibre is subjected to a tensile stress, one would normally expect a realignment of the crystallites as well as a change in the conformation of the polymer chain itself. This paper describes an X-ray method for studying the changes that occur with stress to crystallite stacking inside the fibre.

In cellulosic fibres, the crystallites are arranged with the crystallographic *b*-axis more or less parallel to the axis of the fibre. Hermans *et al.* (1946) have derived a mathematical expression to determine quantitatively the preferred orientation in cellulosic fibres based on the fact that the intensity distribution along the diffraction arc corresponds to the density distribution of the respective crystallographic planes. Creely & Conrad (1965) have developed a diffractometric technique for the evaluation of orientation in cotton from the measurement of the azimuthal width of equatorial reflections.

The spiral structure of cotton was first proposed by Balls (1923). Sisson (1935) had shown a schematic representation of the X-ray diffraction diagram of a cotton fibre in relation to the microscopically visible spiral fibrillar structure. However, further refinements of the above approach have been brought about by the work of Deluca & Orr (1961*a*,*b*). They used the 002 intensity profile of the cellulose fibre to estimate the spirality of various native, decrystallised and mercerised cottons. Using the Deluca & Orr procedure, Kalyanaraman (1978*a*,*b*, 1980) has obtained the orientation and spiral angle from the relatively weaker (040) reflection of the cellulose (Kalyanaraman, 1980). The spiral angle calculations lead to another parameter, namely the angle of crystallite dispersion, which gives information about the changes that occur inside the fibres. This paper discusses the usefulness of X-rays in the study of the variation of the angle of crystallite dispersion with stress and its applicability to the understanding of the elastic nature of fibrous polymers.

Since the fibre has a spiral structure, Deluca & Orr (1961*a*,*b*) separated the experimental azimuthal diffraction curve into two equal Gaussian distribution whose intensity maximums are separated by twice the spiral angle ϕ. The half intensity angle of the two Gaussian distributions denoted by α (Fig. 1) represents the dispersion of the crystallites. These distributions are taken against the azimuthal angle E with the origin at the position of the experimentally observed peak.

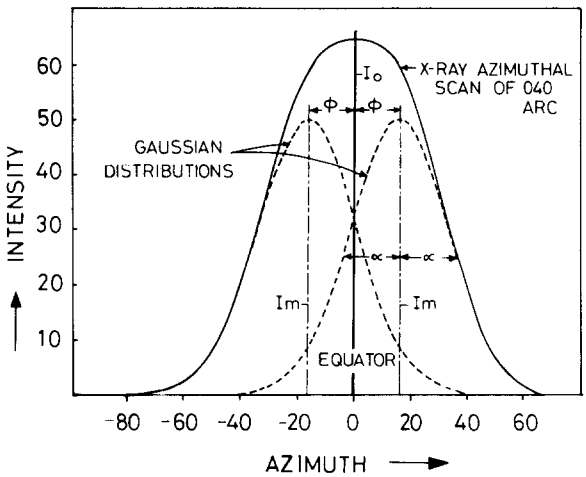

Fig. 1. The two overlapping Gaussian distributions and the resultant diffraction at azimuth zero. The intensity scale is arbitrary.

THEORY — DELUCA & ORR PROCEDURE

Assume that the observed maximum of the intensity distribution is at azimuth E and the two overlapping distributions are located at $E \pm \phi$ were ϕ is the spiral angle. The ordinates of the azimuthal intensity scan curve are the intensities in arbitrary units if the background scatter is subtracted from the observed intensity values.

If the azimuthal intensity is assumed to be due to two overlapping Gaussians represented by I_1 and I_2 then the two Gaussians about the azimuth E are given by

$$I_{1E} = I_m \exp(-H^2(E-\phi)^2) \tag{1}$$

and

$$I_{2E} = I_m \exp(-H^2(E+\phi)^2) \tag{2}$$

where

$$H^2 = \ln 2/\alpha^2 \tag{3}$$

I_m is the net maximum intensity of the Gaussian distribution at $E \pm \phi$ and α is the angle of the half maximum intensity of the distributions. The sum of the two distributions is given by

$$I_E = I_{1E} + I_{2E} \tag{4}$$

and the maximum when $E = 0$ is

$$I_0 = 2I_m \exp(-H^2\phi^2) \tag{5}$$

Using these equations, the ratio of the sum of intensities at azimuths $(E+\phi)$ and $(E-\phi)$ to that at azimuth zero is given by

$$I_E/I_0 = \cosh(2H^2E\phi)\exp(-H^2E^2) \tag{6}$$

Now, if the intensities at azimuths E_1 and E_2 are given by I_{E1} and I_{E2}, then

$$\frac{I_{E1}}{I_0} = \cosh(2H^2E_1\phi)\exp(-H^2E_1^2) \tag{7}$$

If the intensities at azimuths E_1 and E_2 are expressed as ratios of the intensity at $E = 0$, namely

$$\frac{IE_1}{I_0} = I_1 \tag{8}$$

then using eqn (6) a quadratic equation of the form

$$X^2 - 2CX + 1 = 0 \tag{9}$$

is obtained, where

$$X = \exp(2H^2E_1\phi)$$

and

$$C = I_1 \exp(H^2E_1^2)$$

for the intensity at E_1.

The above quadratic equation is solved for X and, using a computer iteration procedure, H and ϕ are obtained so that the values for E_1 agree very well with those obtained for the same parameters observed at E_2. The angle of crystallite dispersion (α) is then calculated from eqn (3).

EXPERIMENTAL

A device was fabricated (Kalyanaraman & Ramakrishnan, 1978) to apply controlled stress to a bundle of fibres, while measuring the azimuthal scan in a monochromatic X-ray beam. The study has been made on cotton fibres and a random sample of the fibres to be studied is taken in the form of a small bundle and, after combing it carefully, a tuft is mounted between paper strips as described previously (Kaly-

anaraman, 1978*a*,*b*, Kalyanaraman & Ramakrishnan, 1978). The thickness of the bundle was chosen so that it was thick enough to give a sufficient intensity of diffracted X-rays and at the same time was thin enough to avoid absorption effects.

Ni-filtered Cu Kα radiation is used and the azimuthal scan of the diatropic (040) diffraction is obtained by using a texture goniometer, a pulse height discriminator and a proportional counter as follows.

The bundle is mounted on a texture goniometer and a 2θ scan of the bundle is made and the reflection (040) is accurately noted. For cellulosic fibres, the angle 2θ for (040) is 34·5°. The intensity at zero position is noted and the intensities at azimuths 15° and 30° on either side of the peak are also measured. The mean values of the intensities are used for the calculations. The background noise is assumed to be linear throughout the azimuthal scan and equal to the intensity at azimuth 90°, where there is no contamination from other reflections. The background noise is estimated on both sides of zero azimuth and the average of these readings is subtracted from the measured intensity values. The angle of crystallite dispersion is calculated by using the Deluca & Orr procedure as outlined previously, with the help of a computer programme.

The bundle is transferred to the Instron machine and is stretched to an elongation of 2%, 4%, 6%, etc., as described by Kalyanaraman & Ramakrishnan (1978). After tensioning and freezing the bundle at the appropriate elongation the bundle holder is transferred to the X-ray equipment and the azimuthal measurements are made. All precautions have been taken to avoid the time bound relaxation phenomena. For each observation, two bundles are used and the average values taken. All experiments have been performed in a conditioned atmosphere of 27 ± 2°C and a relative humidity of 65 ± 2%. Since several bundles are used pertaining to the different elongations it was thought worthwhile to measure the change in elongation and the percentage change in angle of crystallite dispersion. These values are used for subsequent discussions.

RESULTS AND DISCUSSION

The method of deconvoluting the two helical contributions from the observed parameters and evaluating the spiral angle and the angle of

crystallite dispersion has been suggested by Deluca & Orr (1961*a*,*b*). Here we consider the further application of this method and its use in giving information about the internal structure of strained fibrous polymers from the azimuthal scan of the powder diffractometer.

Table 1 gives the correlation of stress and change in elongation with the angle or crystallite dispersion. It is very interesting to note that

TABLE 1
Correlations Between the Elastic Parameters and the Angle of Crystallite Dispersion

	Correlation coefficients	
	Natural	*EDA Treated*
Stress vs. $\Delta\alpha^a$	0·735	0·322
Strain (increase in elongation) vs. $\Delta\alpha^a$	0·747	0·309

[a] α = Percentage decrease in angle of crystallite dispersion.

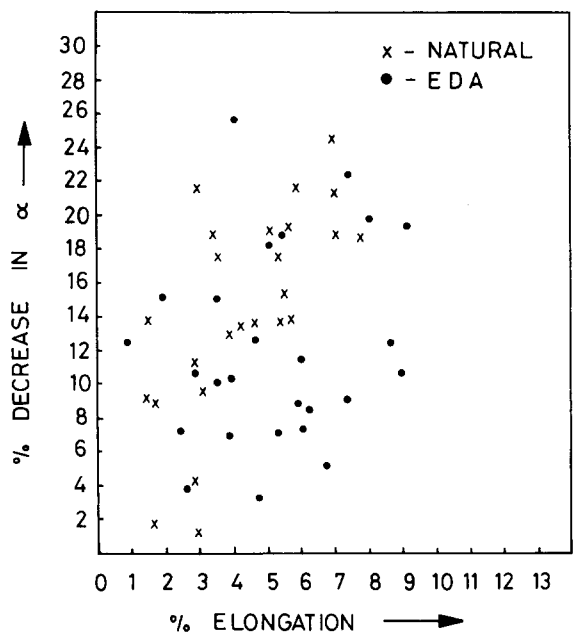

Fig. 2. Comparison of percentage increase in elongation and percentage change in angle of crystallite dispersion for natural and EDA treated cottons.

stress developed and elongation correlate well with the angle of crystallite dispersion in natural cottons but the same correlations are very poor in the ethylene diamine (EDA) treated cotton (Kalyanaraman, 1985). This suggests that EDA treated cottons obey Hooke's law less well than natural cotton fibre indicating thereby a spatial disorder that has developed in the chemically treated fibre. Thus, here, we have an interesting X-ray method by which part of the elastic properties and its relation to internal spatial arrangement can be studied. This is plotted in detail in Fig. 2. In Fig. 2 the increase in elongation is plotted against percentage change (decrease) in α for natural cellulosic fibres and ethylene diamine treated cellulosic fibres. The wide scatter observed in EDA treated cottons is evidence for decrystallization. Similarly, Fig. 3 represents the percentage change in α for the stress developed. It also shows a scatter. Thus, a study of the azimuthal profile of the diffracted intensity gives a method of evaluating the elastic parameters of a fibre as well as a qualitative estimate of the amount of disorder that is present. Further studies with other polymers are in progress.

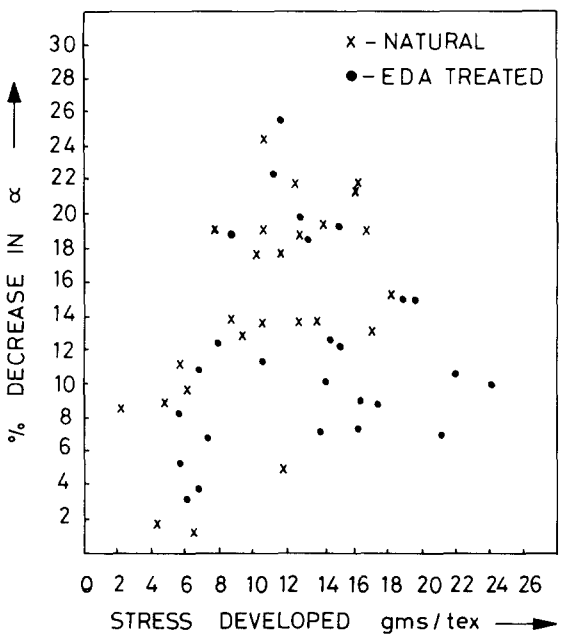

Fig. 3. Comparison of stress developed vs. percentage change in angle of crystallite dispersion for natural and EDA treated cottons.

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