

Tensile properties of biaxially drawn polyethylene

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The tensile properties of simultaneously biaxially drawn solution-crystallized ultra-high molecular weight polyethylene (UHMWPE) films were investigated as a function of draw ratio and were related to the data obtained for uniaxially drawn tapes. The Young's modulus of a biaxially drawn polyethylene film with a random in-plane orientation appears to amount to $\frac{3}{8}$ of the Young's modulus of a tape drawn to the same extent uniaxially. Furthermore, the tensile strength is found to depend solely upon the draw ratio and not upon the drawing geometry since at the point of fracture the orientation in the film has become approximately uniaxial. These relationships are only valid for draw ratios ≤ 10 , whereas for draw ratios > 10 the tensile properties of the biaxially drawn film are not significantly improved in contrast to those of uniaxially drawn tape.

(Keywords: UHMWPE; tensile strength; Young's modulus; simultaneous biaxial drawing; uniaxial drawing)

INTRODUCTION

The tensile properties of uniaxially oriented polyethylene have been extensively studied over the past few decades. The main objective of this research was to achieve high modulus and high strength polyethylene fibres. Capaccio, Ward and co-workers¹⁻⁶, Porter and co-workers⁷⁻¹⁰, Meinel and Peterlin¹¹ and Barham and Keller¹², have examined the solid-state extrusion and drawing of melt-crystallized polyethylene in detail. In contrast, Smith and Lemstra¹³⁻¹⁶ investigated the drawing of solution-crystallized ultra-high molecular weight polyethylene (UHMWPE). Based on the ultra-drawability of UHMWPE crystallized from solution, a process, now often referred to as gel-spinning, has been developed by DSM Research for the production of high strength (3-4 GPa) and high modulus (100-150 GPa) polyethylene fibres¹⁷ on a commercial scale¹⁸.

As well as using solution-crystallized UHMWPE films for the production of uniaxially oriented polyethylene, it is possible to apply a multiaxial drawing process. Despite its industrial importance, relatively little information is available on the structure and properties of biaxially drawn polyethylene films. Minami and co-workers¹⁹ published details on the dependence of Young's modulus on the biaxial draw ratio. They achieved a Young's modulus of ≈ 7 GPa for a film with a random in-plane orientation at a draw ratio of 19×19 . Some publications have appeared on the structure and morphology of biaxially drawn melt-crystallized polyethylene²⁰⁻²² and recently work on the structure of solution-crystallized UHMWPE has been published²³.

Since extensive literature on the tensile properties of uniaxially oriented materials is now available it is worthwhile to examine the relationship between these data and those of biaxially oriented samples.

EXPERIMENTAL

Sample preparation

Solution-crystallized UHMWPE films were prepared by continuously extruding a 15% solution of UHMWPE (Himont HB312, $M_w = 1.5 \times 10^3$ kg mol⁻¹) in decalin. The solution was quenched in water and the resultant film was dried at ambient temperature to a concentration of 80% UHMWPE in decalin.

The undrawn films were simultaneously biaxially stretched to equal elongation in two directions using a stretching frame made by Iwamoto Seisakusho Ltd at a temperature of 110°C, a crosshead speed of 20 mm s⁻¹ and an initial sample dimension of 60 × 60 mm². The same drawing conditions were applied for the uniaxial drawing of tapes. Draw ratios ≤ 10 could be achieved in a single step drawing process. Draw ratios > 10 were obtained by drawing the initial sample approximately three times, reclamping the slightly drawn material and further drawing to the required draw ratio. It was assumed that this discontinuity in the drawing process did not influence the properties of the materials. Draw ratios ranging from 1 to 25 were determined by measuring the displacement of ink marks, placed 1 cm apart onto the specimen before drawing. The thickness of the samples varied between 300 μ m for the original material

and $0.1\ \mu\text{m}$ for the highly drawn film. In this paper a biaxial draw ratio of 10×10 will be referred to as $\lambda = 10$. The terminology 'tape' will be used for material produced by uniaxial drawing and 'film' will be used for material produced by biaxial drawing.

Tensile testing

Room temperature tensile properties were determined from cut strips of film ($100 \times 12\ \text{mm}^2$) using a tensile tester specially made by DSM Research. For measuring film properties the tester was equipped with Zwick clamps (8191N). An initial gauge length of 50 mm was used in each case. The testing speed was $50\ \text{mm min}^{-1}$ and the pre-tension 3 MPa. All stress values were related to the initial cross-sectional area of the film, which was calculated by multiplying the width and the thickness of the test specimens. The thickness was determined using a Millitron mechanical thickness indicator to an accuracy of $0.1\ \mu\text{m}$.

For uniaxially oriented materials a different testing procedure had to be used because the specimens are thicker and have a higher Young's modulus. The tester was equipped with Zwick clamps (8106N). A longer 3 mm wide specimen and an initial gauge length of 100 mm were used. The testing speed was $100\ \text{mm min}^{-1}$ and the pre-tension 50 MPa. The cross-sectional area was calculated from the mass per unit length using a density of $1000\ \text{kg m}^{-3}$.

The Young's moduli quoted in this paper refer to the moduli determined by the maximum of the first derivative of the tensile stress *versus* strain curve. The Young's modulus measured by using this method has appeared to be less dependent on the pre-tension than the conventional secant modulus.

All the tensile properties quoted for the films and for the tapes represent average values of at least five tests.

Postdrawing test

It is now generally accepted that there is a unique relationship between the Young's modulus and the draw ratio for uniaxially oriented polyethylene^{4,10,12,14}. We have therefore attempted to investigate the effectiveness of biaxial drawing compared with uniaxial drawing by performing mixed biaxial and uniaxial drawing.

Figure 1 illustrates the postdrawing procedure. The line at 45° represents biaxial deformation and the vertical lines represent the uniaxial deformation imposed upon the biaxially drawn films in a separate experiment. From Figure 1 it is evident that the total draw ratio of all samples is fixed on 30.

The Young's modulus of this biaxially and then uniaxially drawn sample was measured as described earlier for uniaxially oriented tapes.

Electron microscopy

Transmission electron micrographs (TEM), selected area diffraction patterns (SAED) and electron microdiffraction patterns were obtained using a Philips EM420 electron microscope operated at 120 kV. They were obtained from a film which had been 25×25 biaxially drawn to a thickness of $< 0.1\ \mu\text{m}$. The film could be viewed directly in the microscope without microtoming the sample.

X-ray diffraction

Wide-angle X-ray scattering (WAXS) patterns were

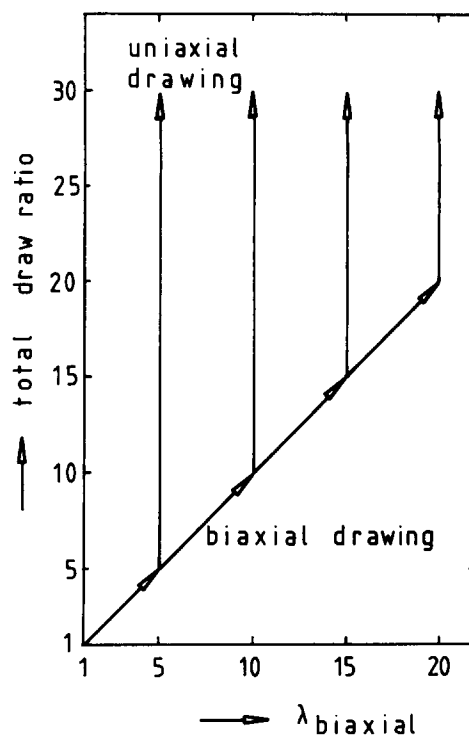


Figure 1 Schematic representation of the drawing conditions in the postdrawing experiment

obtained by a Statton camera with a flat-plate geometry using Ni-filtered $\text{CuK}\alpha$ radiation from a Philips PW1729 generator operated at 50 kV and 40 mA. The patterns for biaxially drawn film were all recorded with the X-ray beam perpendicular to the plane of the sample.

The orientation distribution of samples which were biaxially and then uniaxially drawn was evaluated from WAXS patterns obtained with the X-ray beam normal to the plane of the sample. Densitometer scans were made along the (110) reflection circle in steps of 2° using a Nonius Diffractis densitometer with a spot size of $0.55\ \text{mm}^2$ on the X-ray photographs. The orientation distribution was determined from the full width at half maximum intensity of the (110) reflection.

RESULTS AND DISCUSSION

Tensile properties

Figure 2 shows typical examples of the nominal stress *versus* strain curves of a $\times 10$ uniaxially drawn tape and a 10×10 biaxially drawn film. It should be noted that even though there is a large difference in elongation to break both materials have similar tensile strength.

In Figure 3 the Young's modulus, the tensile strength and the elongation at break are plotted as a function of draw ratio for both uniaxially and biaxially drawn material. A curved relationship is found between the Young's modulus of tapes and the draw ratio, with the slope of the curve increasing with increasing draw ratio. The dependence of modulus on draw ratio for these tapes is different from that found by Smith *et al.*¹⁴ for gel spun fibres. This difference may be accounted for by difficulties in determining the initial draw ratio in solution-crystallized systems.

From the curved relationship between the Young's modulus of films and the draw ratio it appears that above a draw ratio of ≈ 10 the Young's modulus is not

significantly enhanced. Although these data have been found to be reproducible for the different films measured they are not in complete agreement with those of Minami and co-workers¹⁹, who proposed a linear relationship, shown by the dashed line in Figure 3a.

Figure 4 shows the results of the postdrawing experiment. Since the total final draw ratio of the samples is constant (at $\times 30$, Figure 1) a Young's modulus independent of the biaxial draw ratio (dashed line in Figure 4) is expected if the biaxial drawing efficiency is equal to that of uniaxial drawing and if affine deformation

is the predominant deformation mode in the uniaxial drawing step. From the curve in Figure 4 it can be concluded that the initial stage biaxial drawing is nearly as effective as uniaxial drawing. However, at draw ratios > 10 biaxial deformation is significantly less effective than uniaxial drawing. The modulus of the samples with a total draw ratio of 30 decreases as the proportion of biaxial drawing increases.

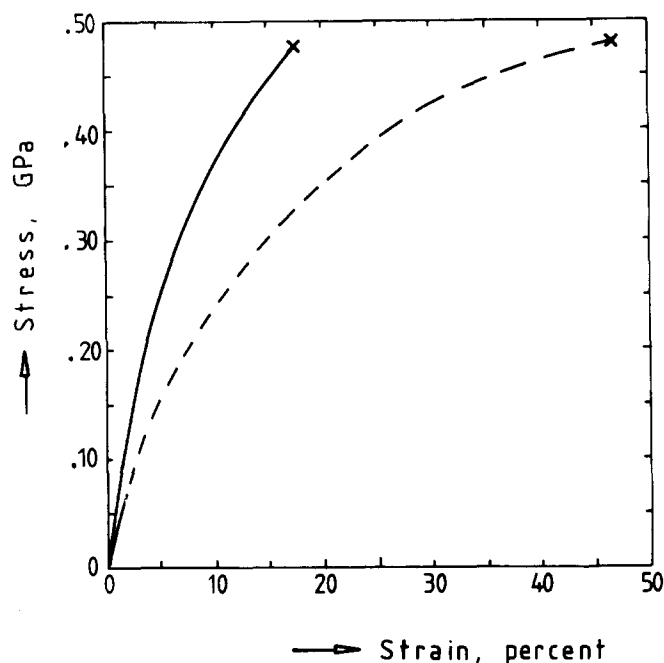


Figure 2 Typical examples of the nominal stress versus strain curves for a $\times 10$ uniaxially drawn tape (—) and 10×10 biaxially drawn film (---)

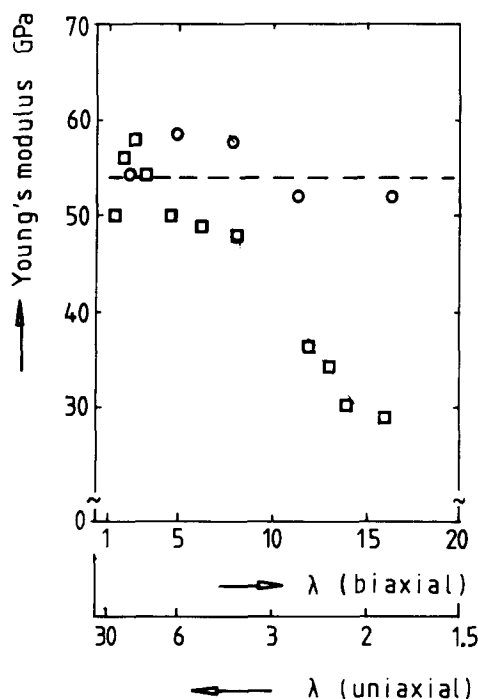


Figure 4 Young's modulus of tapes drawn biaxially and then uniaxially up to a total draw ratio of 30 plotted as a function of the biaxial draw ratio (\square), (\circ). Data for tapes drawn twice uniaxially to a total draw ratio of 30. ---, The relationship if biaxial and uniaxial drawing are equally effective

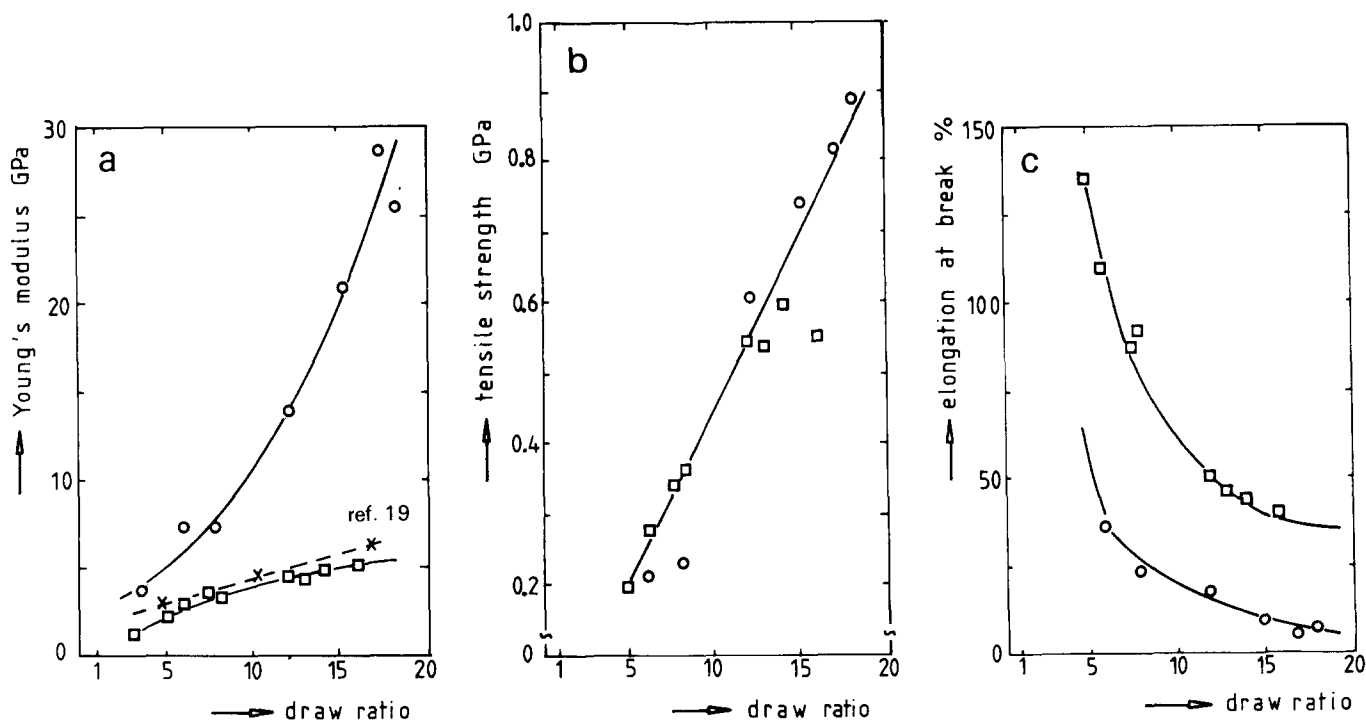


Figure 3 Tensile properties as a function of draw ratio for biaxially drawn films (\square) and for uniaxially drawn tapes (\circ): (a) Young's modulus; (b) tensile strength; (c) elongation at break. ---, Data taken from Reference 19

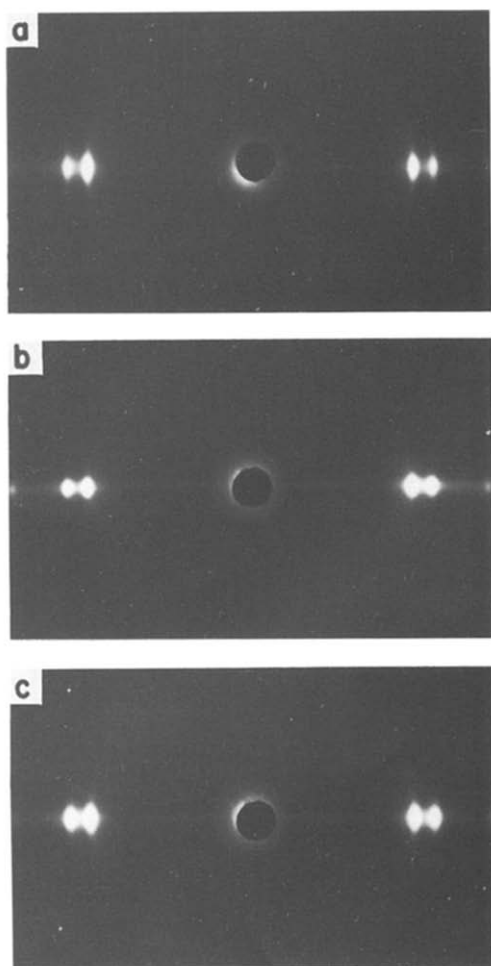


Figure 5 WAXS patterns of tapes drawn first biaxially and then uniaxially up to a total draw ratio of 30. The X-ray beam was normal to the sample surface and the drawing direction is vertical. $\lambda_b =$ (a) 2; (b) 8; (c) 15

WAXS patterns were recorded with the X-ray beam normal to the sample surface (Figure 5) to determine the orientation in the postdrawn films. The full width at half maximum intensity of the (110) reflection was measured from these patterns and appears to be independent of the drawing geometry, suggesting that the crystal orientation is not measurably influenced by the relative proportion of biaxial and uniaxial drawing.

Summarizing the results of the postdrawing experiment, we conclude that for $\lambda \leq 10$ biaxial drawing is as efficient as uniaxial drawing, while for $\lambda > 10$ biaxial drawing is significantly less effective than uniaxial deformation.

Structure

We will now consider some issues concerning the structure of the biaxially drawn film in order to determine the relationship between the tensile properties of biaxially and uniaxially drawn materials. The electron micrographs shown in Figure 6 show that the film is composed of individual fibrils which are oriented randomly in-plane. Note that this ultra-drawn film is somewhat inhomogeneous and areas exist on the micrometre scale possessing a uniaxial fibril orientation. The diffraction pattern (Figure 6b) obtained from a large area (40 μm) shows rings, demonstrating that the random fibril orientation is accompanied by a random orientation of the crystallographic axes, particularly the 002 axis. Additional support

for a random in-plane crystal orientation was obtained from a WAXS pattern showing a random orientation of the (110) reflection in the plane of the film (Figure 7a) and from the fact that the tensile properties are found to be independent of the angle between the two principal drawing directions from which samples were cut.

The crystal orientation of an individual fibril was investigated from electron microdiffraction patterns recorded by using a 2 nm electron probe. From several such diffraction patterns it was concluded that in an individual fibril the *c* axis orientation is parallel to the fibril axis (Figure 8).

The degree of orientation in the fibrils is determined by the draw ratio, in such a way that a film, which is for instance 10×10 drawn, is made up of a mat of fibrils that are $\times 10$ uniaxially drawn. This is confirmed by the results of the postdrawing experiment (Figure 4), which show only a small dependence of the final modulus upon the original biaxial draw ratio for $\lambda \leq 10$.

Relationship between tensile properties and structure

If during biaxial drawing uniaxial deformation on a microscale takes place in the fibrils, then the tensile properties of a film can be related to their uniaxial counterparts via simple geometric conversions. A geometry correction is conventional for modelling the tensile properties of composites using laminate theory^{24,25}. According to this theory the Young's modulus is related

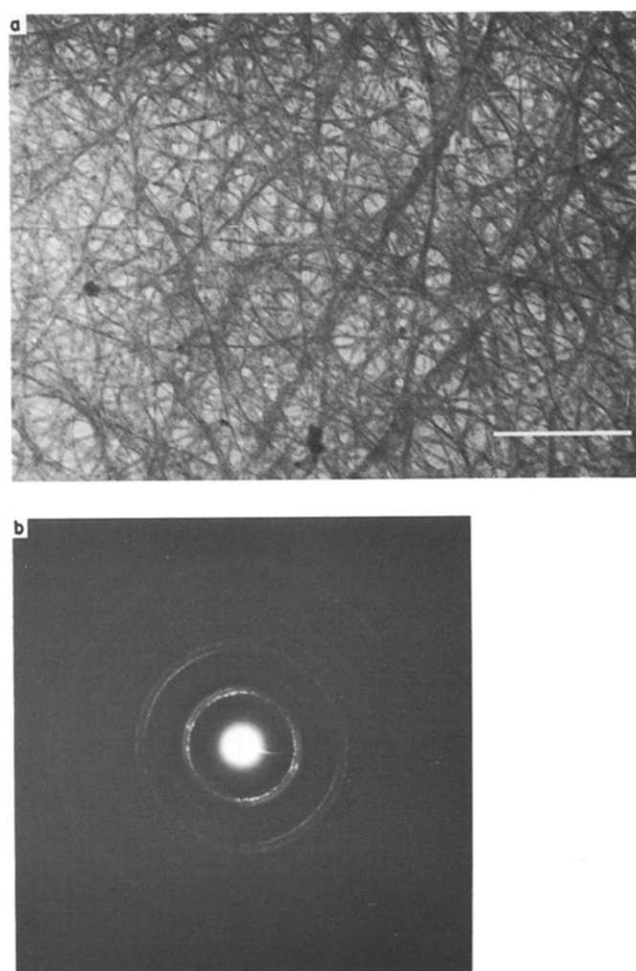


Figure 6 (a) Transmission electron micrograph of a 25×25 biaxially drawn film (scale bar, 1 μm). (b) Diffraction pattern recorded from a 40 μm area

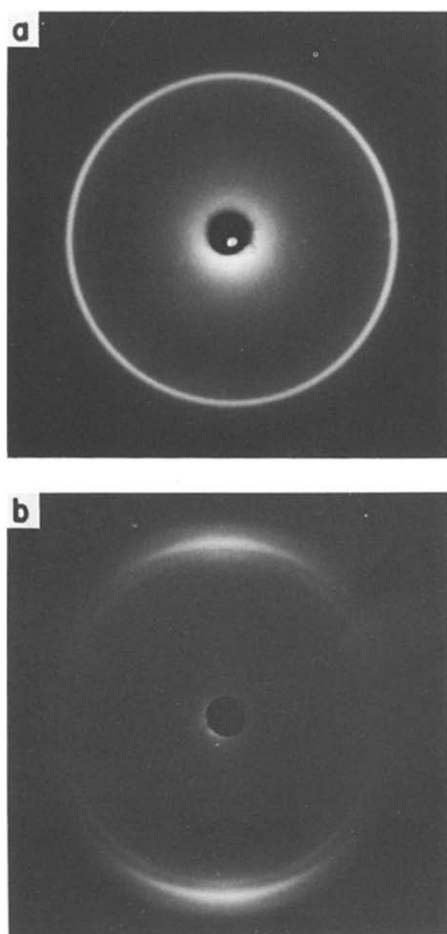


Figure 7 WAXS pattern of a 10×10 biaxially drawn film taken with the X-ray beam normal to the film surface: (a) before tensile testing; (b) after tensile testing

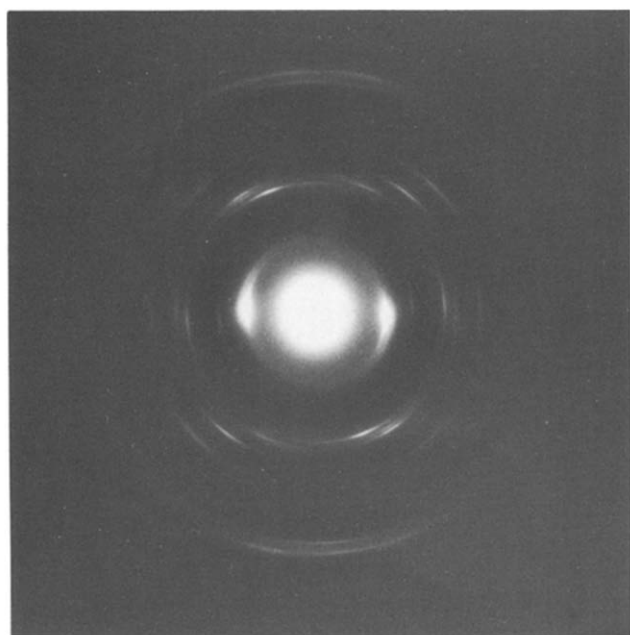


Figure 8 Electron microdiffraction pattern recorded using a 2 nm electron probe (fibril orientation is vertical)

to the fibre orientation distribution by a factor $\cos^4 \theta$, where θ is the angle between the fibres and the applied tension. For a random in-plane fibre distribution the factor has been calculated to be $\frac{3}{8}$ (Reference 26). Taking this correction into account, it is possible to represent

the Young's modulus of a biaxially drawn polyethylene film as a function of draw ratio to that of a uniaxially drawn tape using the relation:

$$E_{\text{biax}}(\lambda) = \frac{3}{8} E_{\text{uniax}}(\lambda) \quad (1)$$

In Figure 9 the relationship given by equation (1) is compared with the experimental data for the Young's modulus of films as a function of draw ratio. It is evident that the description fits the data at low draw ratios ($\lambda \leq 10$), while at higher draw ratios ($\lambda > 10$) the Young's modulus of the biaxially drawn film is significantly less than predicted. The reason for the difference is probably that biaxial drawing at $\lambda > 10$ is less effective than uniaxial drawing, as already shown from the postdrawing experiment (Figure 4). We think that the limited effectiveness is related to the deformation mechanism and this will be extensively discussed in a forthcoming paper²⁸.

We emphasize that the relationship given by equation (1) is only valid when dealing with individual fibrils possessing an almost isotropic Young's modulus²⁶. For a fibrillar structure composed of units with highly anisotropic properties the laminate theory can only be used if the difference between the axial modulus of the fibres and the modulus of the matrix is not too large²⁴⁻²⁶.

The ultimate Young's modulus of a biaxially drawn film has been calculated by Bastiaansen *et al.*²⁷. They took a model of an ideal film composed of an aggregate of perfect chain-extended crystals arranged with the *c* axis in the plane of the film. These crystals were assumed to have the mechanical properties given by the crystal stiffness tensor. They were able to calculate a maximum attainable Young's modulus for a two-dimensional isotropic polyethylene film to be between 8 and 12 GPa, depending on the *a* and *b* axis orientation. This theoretical limit of about 10 GPa is plotted as a horizontal dashed line in Figure 9. It can be seen that the experimental data on the biaxially drawn film do not exceed the 10 GPa predicted by Bastiaansen *et al.*²⁷.

It is now worth considering what factors control the tensile strength of films. Figure 7 shows WAXS patterns for a film before and after tensile testing. It shows that

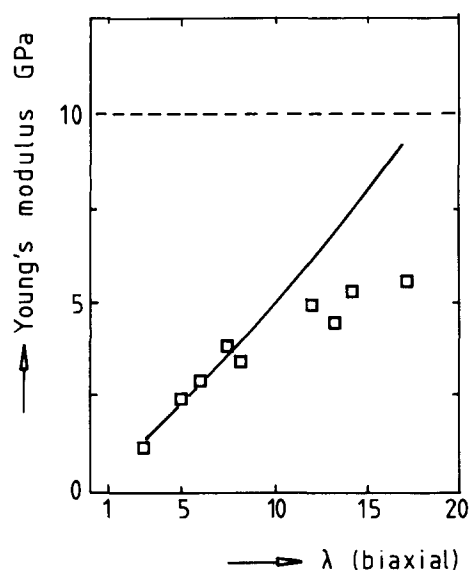


Figure 9 Young's modulus of biaxially drawn films calculated as $\frac{3}{8}$ of the modulus of uniaxially drawn tapes compared with the experimental data. ---, Theoretical model prediction for Young's modulus taken from Reference 27

a uniaxial orientation has developed when the film breaks and so a correction for geometry may not be necessary. Therefore, one might expect that the tensile strength of the biaxially drawn films is similar to that of the uniaxially drawn tapes at a given draw ratio. Figure 3b shows that there is indeed a close relationship between the tensile strength and draw ratio for both types of samples, at least for draw ratios of up to ≈ 10 .

CONCLUSIONS

For draw ratios ≤ 10 the tensile properties of a biaxially drawn polyethylene film can be predicted as a function of draw ratio from the relationship between the properties and draw ratio for uniaxially oriented samples. It has been found that the Young's modulus of a biaxially drawn film is $\frac{3}{8}$ of that of the uniaxially drawn tape. The tensile strength of the two types of material is found to be similar for a given draw ratio.

At draw ratios > 10 these relationships no longer hold due to the lower effectiveness of biaxial drawing than of uniaxial drawing.

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