

Porous biaxially drawn ultra-high molecular weight polyethylene films

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The morphology and tensile properties of porous biaxially drawn ultra-high molecular weight polyethylene films were investigated as a function of draw ratio and compared to the properties obtained for non-porous reference samples. Biaxially drawn porous films possessing a porosity of over 80% for $\lambda \geq 3$ are composed of a network of uniaxially oriented fibrils similar to biaxially drawn non-porous films. However, the fibrils in the porous films possess a fibre texture whereas in the non-porous films a mixed (100) and (110) texture can be observed. Both the Young's modulus and the tensile strength of porous biaxially drawn films are relatively poor compared to the tensile properties of non-porous films. This is due to the modulus being governed by the deformation of a loose fibrillar network, rather than by the properties of the fibrils. The tensile strength is reduced by the inhomogeneous structure and additionally by the non-uniaxial orientation of the fibrils when the film fractures.

(Keywords: UHMW-PE; porous; biaxial drawing; Young's modulus; tensile strength; morphology)

INTRODUCTION

The deformation mechanisms, morphology and tensile properties of biaxially drawn polyethylene have been studied by several workers.¹⁻⁶ The principal objectives of their research were to understand the deformation processes^{1,4,6} and to determine the relationship between the tensile properties and the morphology of the films^{2,3,5}. To our knowledge these reports¹⁻⁶ have been concerned with the morphology and properties of semi-transparent non-porous biaxially drawn polyethylene, although this is not explicitly stated in all cases.

Nowadays there is a growing interest in polymer products possessing a degree of porosity. The patent of Gore⁷ concerning porous polytetrafluoroethylene (PTFE) films is representative of a number of patents describing both the production of porous polymer films prepared by drawing and the use of these products, for example in breathable waterproof articles. The production of porous polyethylene films is claimed by Celanese Corporation in a series of patents⁸. All the processes comprise a combination of cold and hot uniaxial drawing of non-porous melt-crystallized polyethylene. Recently it was found at DSM Research that porous ultra-high molecular weight polyethylene (UHMW-PE) films can be manufactured by solid-state biaxial drawing of porous solution-crystallized UHMW-PE films⁹. The porosity of these precursor films has been induced by geometrical constraints during the removal of the solvent after fixation of the polymer network by gelation.

In the present work the morphology and the tensile properties of biaxially drawn porous UHMW-PE films have been studied as a function of draw ratio. The morphology has been studied by density measurements, scanning electron microscopy and wide-angle X-ray scattering. Conventional tensile testing has been used to determine the Young's modulus and the tensile strength. The results have been compared with those obtained for non-porous reference films.

EXPERIMENTAL

Sample preparation

Solution-crystallized UHMW-PE films were prepared by continuously extruding a 15% solution of UHMW-PE (Himont HB312CM, $M_w = 1.5 \times 10^3 \text{ kg mol}^{-1}$) in decalin. The solution was quenched in water and the resultant film was dried at room temperature preserving its surface dimensions. This resulted in a porous film. Preliminary experiments were performed to determine the conditions under which non-porous reference samples could be prepared. It was found that by compressing the porous films at a temperature of 120°C for 10 min, using a pressure of 10 MPa, good translucent films could be produced. Compression improved the connectivity between the fibrils without melting the polyethylene crystals.

Both the porous and the non-porous samples were drawn biaxially to equal elongations in two directions using a stretching frame made by Iwamoto Seisakusho Ltd. The initial sample dimensions were $60 \times 60 \text{ mm}^2$. A crosshead speed of 300 mm min^{-1} and a temperature of

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120°C were employed for the drawing process. In this paper a biaxial draw ratio of 5×5 will be referred to as $\lambda = 5$. The exact draw ratios, varying between 1 and 10, were determined in the usual way by measuring the displacement of ink marks placed onto the specimen 1 cm apart prior to drawing.

Density

The overall density (ρ) was calculated as the mass of the specimen divided by its volume. The volume was determined from the product of the surface area and the thickness of the specimen. The thickness was measured to an accuracy of $0.1 \mu\text{m}$ using a Millitron mechanical thickness indicator.

This instrument was specially adapted for measuring typical samples with a low modulus of compression, which involved using a large contact area and low pressure.

Porosity

The porosity was calculated using the following equation:

$$\text{porosity (\%)} = \frac{\rho_0 - \rho}{\rho_0} \times 100\% \quad (1)$$

where ρ is the overall density and ρ_0 is the matrix polyethylene density. The crystallinity was assumed to be approximately 80% based on d.s.c. measurements at different draw ratios. Consequently a value of $\rho_0 = 970 \text{ kg m}^{-3}$ was used in the calculations.

Electron microscopy

Scanning electron micrographs were obtained using a Cambridge Stereoscan 200 electron microscope operated at 10 kV. A 20 nm thick Au/Pd layer was sputtered onto the specimens before examination to render them conductive.

Tensile testing

The room temperature tensile properties were determined from 12 mm wide strips of film using a tensile tester developed by DSM Research. An initial gauge length of 100 mm and a testing speed of 100 mm min^{-1} were employed in each case. The effective cross-sectional area was calculated from the mass per unit length using a density of 970 kg m^{-3} . Hence, the tensile properties quoted for the porous films are corrected for porosity and comparable with the values quoted for transparent ones.

Post-drawing test

The tensile properties of the individual fibrils in a biaxially drawn film were investigated by performing mixed biaxial and uniaxial drawing in such a way that a uniaxial chain axes orientation was eventually achieved. The total draw ratio of all the samples was fixed at 15. Tensile testing of these biaxially and subsequently uniaxially drawn strips was performed as described above and the tensile properties of the fibrils were determined as in a previous paper⁵.

X-ray diffraction

Wide-angle X-ray scattering (WAXS) patterns were obtained using a Statton camera with a flat-film geo-

metry, Ni-filtered $\text{CuK}\alpha$ radiation from a Philips PW 1729 generator operated at 50 kV and 40 mA was employed. Diffraction patterns were obtained at room temperature with the incident X-ray beam both normal and parallel to the sample surface.

Texture measurements were carried out using a computer-controlled Siemens diffractometer and Ni-filtered $\text{CuK}\alpha$ radiation of a rotating anode generator (7 kW developed by STOE). The intensity of the X-rays diffracted from the (110) and (200) lattice planes was measured. The pole figures were calculated from the experimental data using commercial Siemens TEX11 software. The measured data were corrected for background radiation, sample thickness, absorption coefficient and the defocussing effect. The intensities were then normalized and the pole figures were plotted. Details of texture measurements can be obtained from reference 6.

Small-angle X-ray scattering (SAXS) patterns were determined using a Kiessig camera equipped with a very fine pinhole collimation system. Ni-filtered $\text{CuK}\alpha$ radiation generated at 50 kV and 40 mA from a Philips PW1730 generator was employed. The sample-to-film distance was 400 mm and diffraction patterns were obtained with the incident X-ray beam normal to the sample surface.

RESULTS AND DISCUSSION

Morphology

The dependence of porosity of the biaxially drawn films upon the draw ratio will be considered first. The porosity of the undrawn solution-crystallized UHMW-PE film was measured to be 60%. It can be seen from *Figure 1* that the porosity increases dramatically in the initial stages of drawing ($\lambda \leq 3$). This increase in porosity can be related to an increase in pore diameter visualized by the scanning electron micrographs of the biaxially drawn films in *Figure 2*. For $\lambda > 3$ the porosity decreases slightly, although the diameter of the pores still increases. This decrease in porosity may be explained by transverse contraction compacting the porous structure during

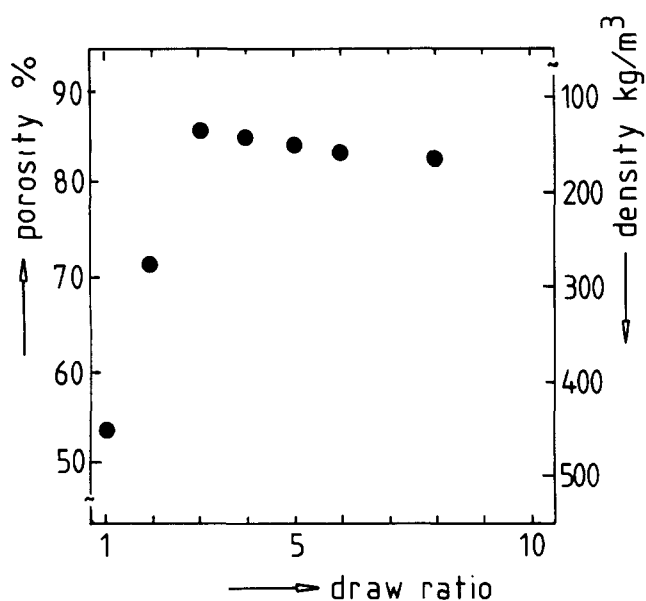


Figure 1 Porosity and density as a function of draw ratio for biaxially drawn porous UHMW-PE films

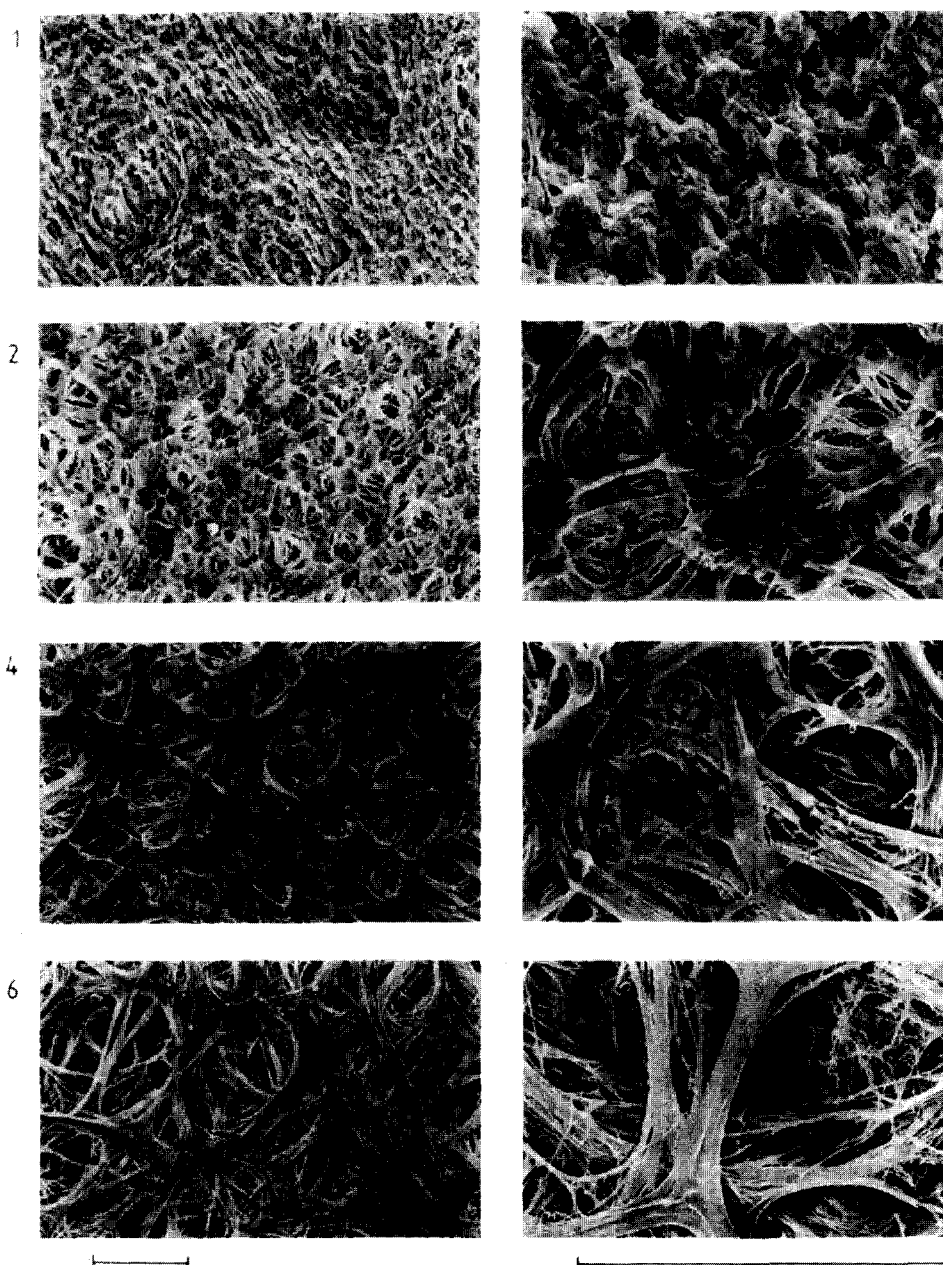


Figure 2 Scanning electron micrographs, at two magnifications, of the surface of biaxially drawn porous UHMW-PE films as a function of draw ratio, as indicated on the left. Scale bars represent $100\ \mu\text{m}$

biaxial drawing. The porosity of transparent reference samples is approximately zero for all draw ratios and so it is not shown in *Figure 1*.

The scanning electron micrographs show that porous biaxially drawn films are composed of individual fibrils, which are oriented randomly in-plane. The diameter of the fibrils varies between 3 and $10\ \mu\text{m}$ and their length between 15 and $100\ \mu\text{m}$ depending mainly upon the draw ratio. In the initial stages of drawing ($\lambda = 2$) fibrils are formed on the equators of the pores. However, the material connecting the fibrils is still undrawn for $\lambda = 2$. This inhomogeneous deformation on a microscopic scale is explained by the stress concentrating effect of the pores. It is well known from the work of Inglis¹⁰ and Kolosoff¹¹ that if a force is applied on an isotropic material with holes there is a stress concentration at the equators of the holes. It is not surprising therefore that during drawing of a porous film, fibrils are generated on the edges of the pores, whereas the material connecting the

fibrils is virtually undeformed. Furthermore it should be noted that although deformation on a microscopic scale is inhomogeneous, macroscopic deformation of the samples is homogeneous due to multiple necking around a large number of pores.

For $\lambda \geq 6$ the macroscopic homogeneous films possess a uniform fibrillar structure as can be seen from the electron micrographs. However, a scanning electron micrograph cannot be used to determine the exact draw ratio of the polyethylene fibrils and so it is difficult to determine the deformation of the individual crystals.

Tensile properties

The Young's modulus is shown as a function of draw ratio for both porous and non-porous biaxially drawn films in *Figure 3a*. The modulus of the porous films, even when corrected for porosity, is significantly lower than that of the non-porous films. In principle there may be

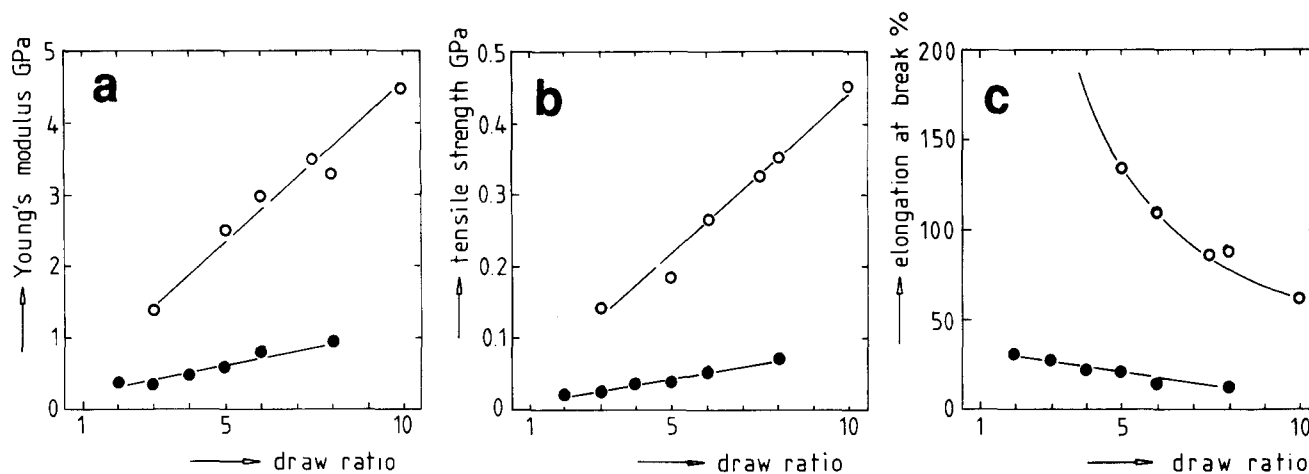


Figure 3 Tensile properties as a function of draw ratio for biaxially drawn porous UHMW-PE films (●). Data for non-porous UHMW-PE films (○) are shown as a reference. (a) Young's modulus; (b) tensile strength; (c) elongation at break. Data are corrected for the porosity of the samples

two reasons for this difference in film modulus:

- (1) the Young's modulus of the fibrils is lower in a porous than in a non-porous film and/or
- (2) the porous film behaves as a loose fibrillar network rather than a tight fibrillar structure when a force is applied to the film.

In order to discriminate between these two possibilities, the so-called post-drawing experiment was employed to deduce the inherent fibril stiffness⁵. A $\times 5$ biaxially drawn porous and a $\times 5$ biaxially drawn non-porous film were exposed to an extra uniaxial drawing step in such a way that the total draw ratio of the resulting strips was 15. The Young's modulus of both strips, which possess a uniaxial orientation, was found to be 15 GPa. Therefore, it is concluded that the Young's modulus of the individual fibrils is equal in both types of material and that a porous film may be considered as a loose network of relatively stiff fibrils with poor connectivity. This mechanical behaviour can be contrasted to that of the dense non-porous films where there is good connectivity and for which the modulus has been shown to be related to the modulus of uniaxially drawn tapes through a simple correction for the drawing geometry⁵.

In *Figures 3b* and *3c* the tensile strength and the elongation at break, respectively, are illustrated as a function of draw ratio for both porous and non-porous films. It is evident that both the tensile strength and the elongation at break are lower in porous films than in non-porous films. At least two explanations can be given for this difference in tensile strength:

- (1) the tensile strength of the fibrils in porous films is lower than in non-porous films and/or
- (2) biaxially drawn porous films fracture at relatively low strains and so a uniaxial fibril orientation does not develop, in contrast to the non-porous films⁵.

The tensile strength of the fibrils was investigated using the post-drawing test. The tensile strength of a porous film, exposed to an extra uniaxial drawing step, was found to be significantly lower than that of the non-porous post-drawn specimen. The low tensile strength of the fibrils can be explained by either the spread in local draw ratio caused by the initially inhomogeneous deformation or the presence of microvoids in the sample. An attempt was made to determine the presence of initial microvoids

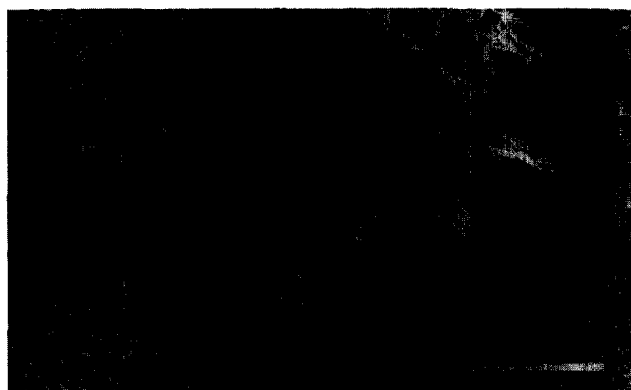


Figure 4 Scanning electron micrograph of a $\times 6$ biaxially drawn porous UHMW-PE film after tensile testing. Scale bar represents 100 μm

in the post-drawn samples by means of small-angle X-ray scattering, but no microvoid scattering could be detected from the SAXS patterns. Hence, the range in local draw ratios is the most likely reason for the limited tensile strength of the fibrils in a porous film and consequently the strength of the entire film.

The orientation of the fibrils at the point of fracture in a porous film can be evaluated from an electron micrograph of a fractured film (*Figure 4*). The fibrillar orientation appears to be far from uniaxial, consistent with the relatively small elongation at break for porous films. In contrast, the orientation of the chain axes and consequently the orientation of the fibrils is shown to be uniaxial at the time a non-porous film breaks⁵. An additional factor giving rise to the low tensile strength of the porous films may be the low degree of fibrillar orientation at break.

Crystal orientation

Figure 5 illustrates WAXS patterns recorded with the incident X-ray beam both normal and parallel to the surface of the porous film. The patterns recorded with the beam normal to the film show a random orientation of the normals to the (110) and the (200) crystal planes around the film normal, as would be expected for simultaneous biaxial drawing. Patterns recorded with the beam parallel to the surface indicate a gradual transition of the random orientation into a preferred orientation

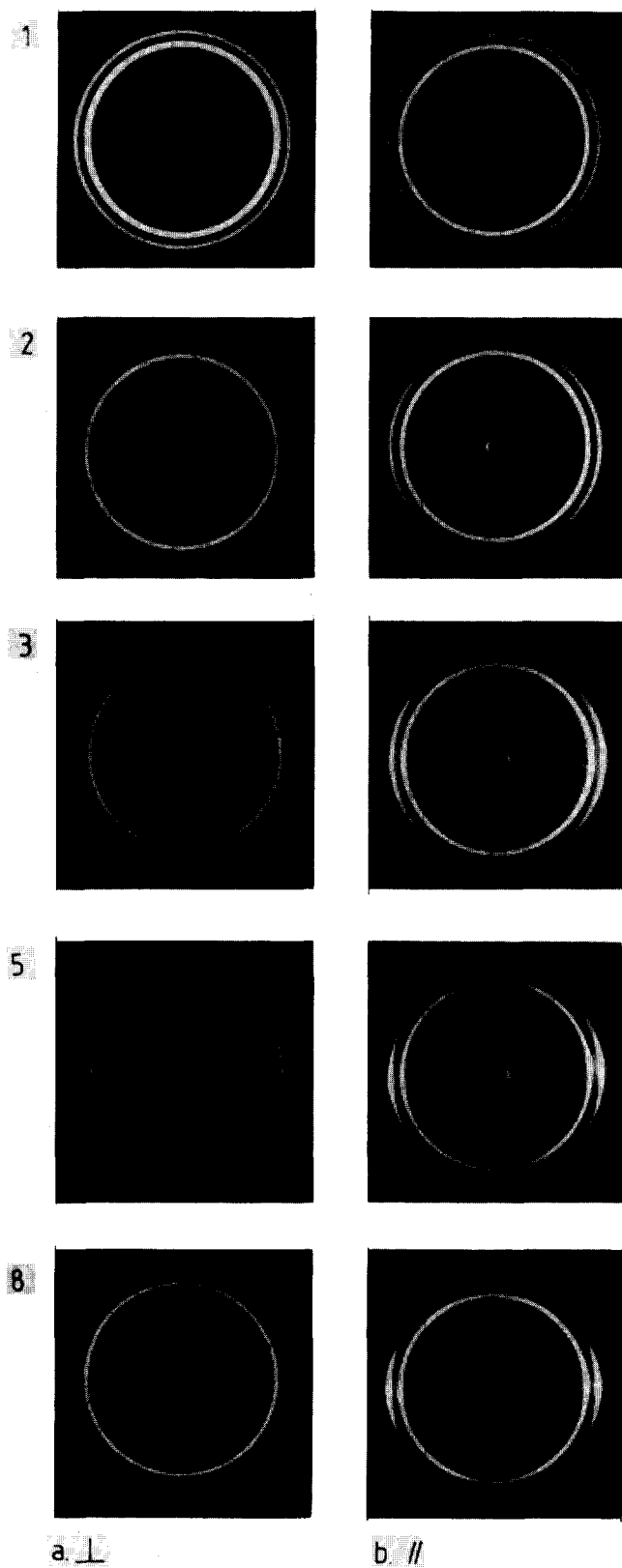


Figure 5 WAXS patterns of biaxially drawn porous UHMW-PE films recorded with the incident X-ray beam normal (a) and parallel (b) to the film surface. The direction normal to the film plane is horizontal and the draw ratio is indicated on the left in each case

with the normals to the (110) and (200) crystal planes rotating towards the equator. This gradual transformation seems to contradict the inhomogeneous deformation observed for the scanning electron micrographs (Figure 2). However, it should be emphasized that the WAXS patterns recorded, using an incident X-ray beam with a

diameter of 500 μm , show an average of the different crystal orientations in a sample and therefore they cannot be used to discriminate between homogeneous and inhomogeneous deformation on the microscopic scale.

The WAXS patterns indicate the development of a fibre texture and this is further supported by pole figures showing (110) and (200) intensity maxima in the centre of the (110) and the (200) pole figures respectively (Figure 6). The fibre texture in porous films is explained by the fibrils deforming like separate fibres undergoing unconstrained uniaxial deformation. In contrast, biaxially drawn non-porous films possess a mixed (100) and (110) texture⁶ for $\lambda \geq 6$.

An alternative way of explaining the difference in drawing behaviour and texture development might be the possibility of different deformation mechanisms for

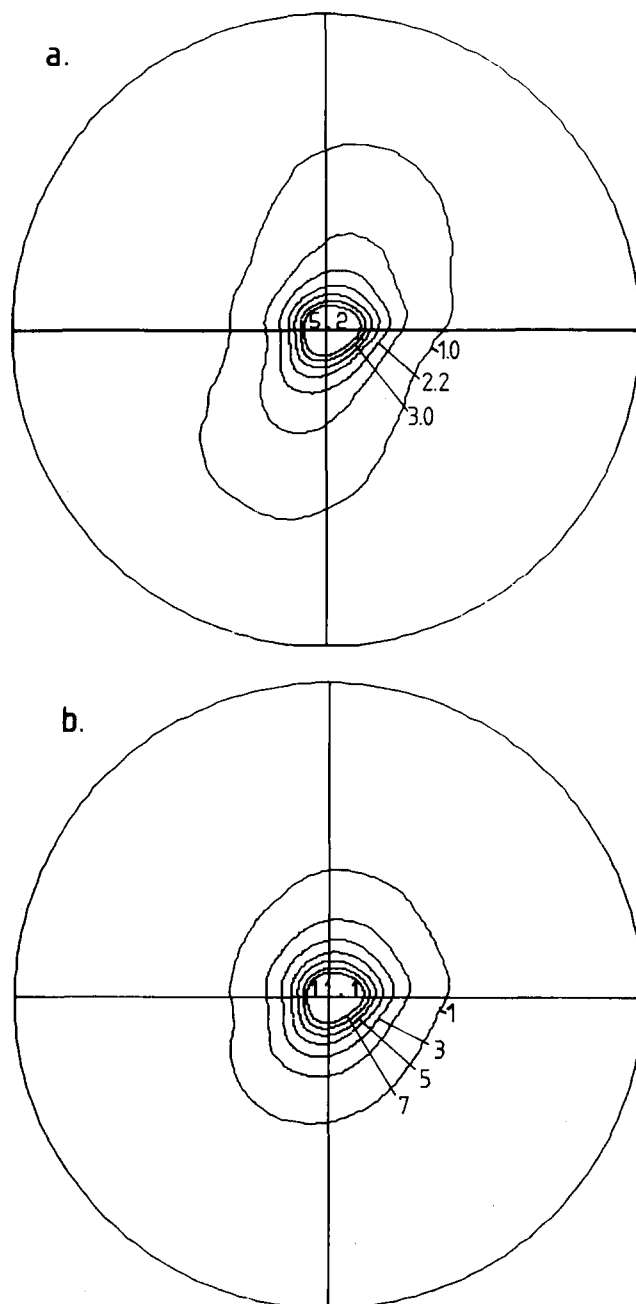


Figure 6 Pole figures of a $\times 5$ biaxially drawn porous UHMW-PE film. The direction normal to the film surface is centred. Contour intensity levels are indicated. (a) (110) reflection and (b) (200) reflection

porous and non-porous films. However, this explanation is rather unlikely since the crystallization conditions and consequently the crystal morphology are identical for the porous and the non-porous films.

CONCLUSIONS

Porous solution-crystallized UHMW-PE films can be drawn biaxially to obtain a degree of porosity over 80%. In the initial stages of drawing ($\lambda = 2$) the deformation in a porous film proceeds inhomogeneously on a microscopic scale due to local stress concentrations caused by the pores. The initially isotropic porous film is gradually transformed into a film composed of fibrils with a fibre texture which can be determined from X-ray diffraction measurements.

The Young's modulus of porous films is governed by the deformation of a loose network of highly oriented fibrils, rather than by the modulus of the individual fibrils. The tensile strength of the films is reduced by the low tensile strength of the fibrils and additionally by the non-uniaxial orientation of the fibrils when the film fractures.

Although the biaxially-oriented porous films have relatively poor tensile properties, they are potentially very useful for a variety of membrane applications, such as

battery separators and breathable textiles. In such applications the films are often subjected to deformation and so a full understanding of their structure and properties is essential.

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