Plastic deformation of thin films of ultra-high-molecular-weight polyethylene

H.-J. Kestenbach
Universidade Federal de São Carlos, Departamento de Engenharia de Materiais, 13560 São Carlos, Brazil

and J. Petermann*
Universität Dortmund, Fachbereich Chemietechnik, D-44221 Dortmund, Germany
(Received 17 March 1994)

A very simple plastic deformation process was applied to thin films of ultra-high-molecular-weight polyethylene (UHMWPE) prepared from dilute solution and mounted on standard 100 mesh electron microscopy grids in order to study the changes in supermolecular morphology which occurred during necking. Starting from an as-cast spherulitic type of microstructure, processes such as macromolecular reorientation, the destruction of lamellar crystallinity and the initial stage of microfibril formation were directly observed in the transmission electron microscope. Microfibrils were found to be composed of 10 nm thick crystals, in contrast to an initial lamellar thickness of 20 nm for the original microstructure. It is believed that the new crystalline morphology was generated by a process of complete lamellar destruction followed by the stress-induced recrystallization of extended chain segments.

(Keywords: UHMWPE; plastic deformation; transmission electron microscopy)

INTRODUCTION

High modulus fibres can be prepared from semicrystalline polymers by plastic deformation during which the necking process offers the opportunity of high drawing ratios required for extension and alignment of the macromolecules parallel to the fibre axis. In the case of ultra-high-molecular-weight polyethylene (UHMWPE), excellent tensile properties can be reached which combine a Young's modulus of 50 to 125 GPa with a tensile strength of 1.0 to 3.5 GPa and a total elongation of 3–7%[1].

Since the beginning of scientific study of the phenomenon, structural aspects of necking have been associated with a stress-induced destruction of the crystalline phase[2,3]. Electron microscopic observations in particular revealed the destruction of lamellar morphologies which, during the course of necking, were replaced by new fibrillar crystals. This morphological transformation of the crystalline phase is generally considered to occur as described by the Peterlin model[4]. During the first stage of deformation, chain-folded crystal lamellae rotate in order to be sheared into separate crystal blocks which align their molecular direction parallel to the applied stress. During the second stage, the crystal blocks themselves become aligned in the tensile direction, forming chain-extended fibrils characterized by their periodic repetition of crystalline and amorphous sections.

The Peterlin model, in principle, suggests a reorganization of the previously existing crystal phase by purely mechanical means. Other mechanisms were proposed, starting with a complete destruction of the crystalline phase which, at a later stage, would re-emerge in the form of new oriented crystals, due to a separate process of recrystallization under stress[5–14]. The initial loss of crystallinity, in this case, could occur due to the deformation-induced increase in temperature which would lead to localized melting events or could be the complete mechanical destruction of the lamellae, which would occur at the actual deformation temperature. This alternative, termed decrystallization by mechanical means, has recently been observed[15] as the result of plastic deformation of oriented thin films of HDPE (high-density polyethylene), and on amorphous and crystalline[16] films of isotactic polystyrene blended with amorphous atactic polystyrene.

In the present investigation, transmission electron microscopy was used in order to follow the structural transformations which were introduced by plastic deformation in UHMWPE with a spherulitic morphology. It was hoped that careful measurements of the crystal size before and after necking might yield additional information with respect to the Peterlin model and the alternative mechanisms of recrystallization under stress.

EXPERIMENTAL

Materials and processing

Powder samples of UHMWPE with a molecular weight of 3.5×10^6 g mol^{-1} were obtained from Polialden Petroquimica S.A., Brazil. Thin films for electron microscopy were prepared from dilute solutions of 0.05–0.2% in decalin, cast on phosphoric acid at 200°C, and crystallized during air cooling.

* To whom correspondence should be addressed

0032-3861/94/24/5217–08

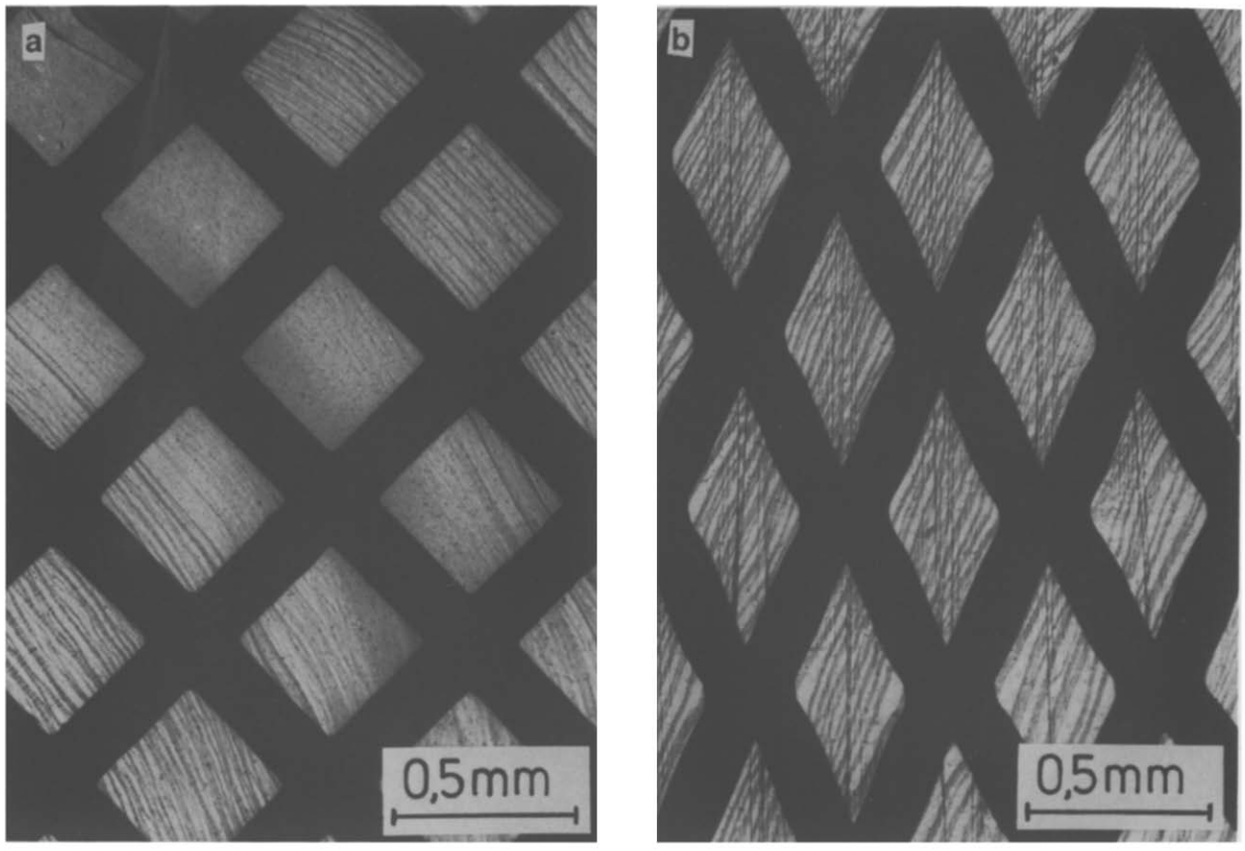

Figure 1 Thin film of UHMWPE mounted on copper electron microscope grid, (a) before and (b) after deformation

Plastic deformation

Thin films were mounted on standard copper electron microscope grids (mesh 100) and plastically deformed in a tensile holder constructed similarly to the ordinary side-entry deformation holder used as an attachment to the transmission electron microscope (*Figure 1*). For plastic deformation at elevated temperature (100°C), the shaft of the deformation holder was inserted into a simple laboratory oven maintained at the required temperature.

Electron microscopy

UHMWPE films were observed before and after plastic deformation in a Philips EM-400 T electron microscope, operated at 120 kV. Appropriate bright-field and dark-field techniques as well as electron diffraction were used in order to study the response of the crystal to plastic deformation. Radiation damage to the crystalline phase was minimized by studying 'virgin' areas where electron beam irradiation had only started at the moment of photographic exposure.

RESULTS

Initial morphology

Crystallization from dilute solution led to a typical non-oriented lamellar morphology (*Figure 2*). Both the characteristic Bragg contrast in bright field, *Figure 2a*, as well as the fragmented aspect of the dark field image, *Figure 2b*, indicated the twisted state of the lamellae. Using both forms of crystalline contrast, a minimum width of 20 nm was determined by careful measurements which should correspond to the actual thickness of lamellae viewed in an edge-on orientation. Electron diffraction patterns, *Figure 3*, confirmed the presence of spherulitic crystallization with the so-called 'b-morphology', previously observed to be the preferential crystal orientation in thin films of normal polyethylene and characterized by a higher (200) intensity in the plane of the foil, *Figure 3a*, as opposed to a higher (110) intensity for a specimen tilt of 30°, *Figure 3b*.

Plastic deformation and the necking phenomenon

The macroscopic sample deformation was limited to about 50% of linear elongation, due to the premature rupture of the copper support grids. On a microscopic scale, however, film deformation was found to be very heterogeneous, reaching rather elevated drawing ratios in certain areas which could allow the observation of necking as a localized phenomenon, *Figure 4*. At the same time, fine-scale film folding occurred in those areas that remained free from necking, due to film contraction perpendicular to the drawing direction. An interesting observation was the disappearance of these folds under high-intensity irradiation, *Figure 5*, indicating a process of relaxation caused by electron beam heating.

Transformation of the crystalline phase

The main effect of plastic deformation after necking, as expected, was the alignment of the macromolecules parallel to the drawing direction, readily identified from the appearance of a typical fibre orientation on electron diffraction patterns (*Figure 6*). Morphologically, such alignment of the crystalline phase was accompanied by the disappearance of lamellae structures which, after

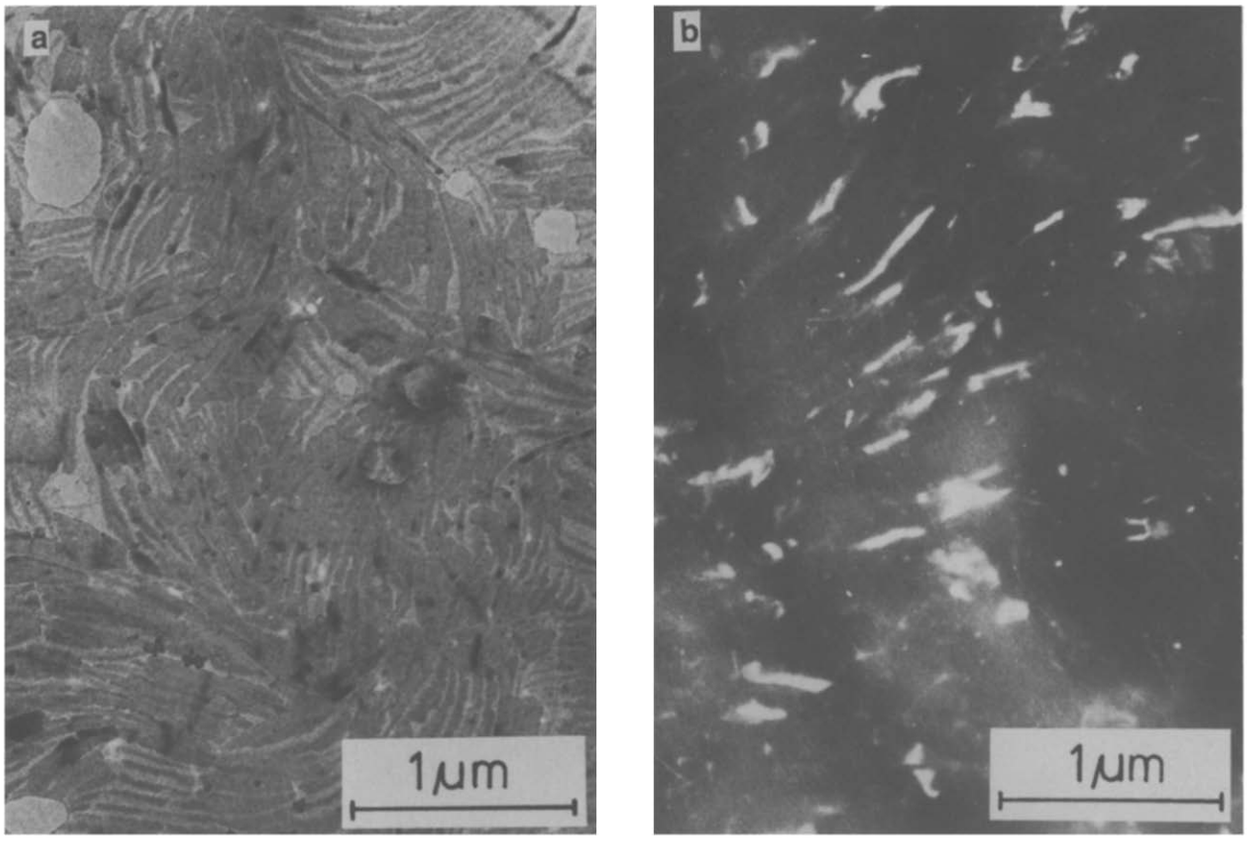

Figure 2 Lamellar morphology of a thin film of UHMWPE crystallized from solution. (a) Bright field; (b) dark field

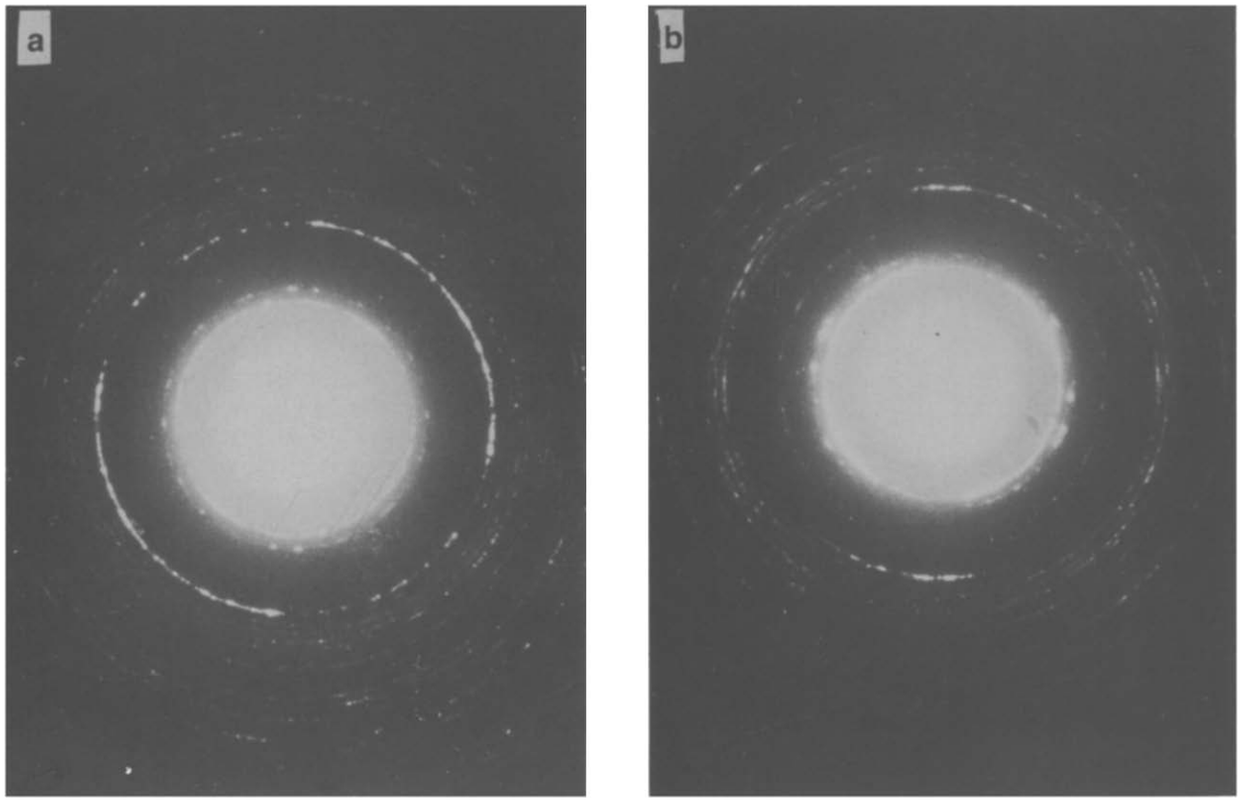

Figure 3 Electron diffraction patterns from a thin film of UHMWPE crystallized from solution. Sample holder in horizontal position in (a), inclined to 30° in (b)

necking, were replaced by new crystalline regions of smaller size (*Figure 7*). Frequently, these new crystals themselves were observed to align parallel to the drawing direction (*Figure 8*). Careful measurement of the size of these new crystals, always performed in 'virgin' areas (electron irradiated only during photographic exposure), yields a characteristic dimension of 10 nm in the direction of drawing, equivalent to only half of the previous lamellar thickness.

The destruction of the crystalline phase during necking was also confirmed under bright field conditions by the total absence of lamellar phase contrast on defocusing, *Figure 9a*. As shown in *Figure 9b*, however, a new aligned lamellar contrast appeared during subsequent electron beam irradiation, apparently as the result of some relaxation mechanism which tended to re-establish the original film dimensions (see also *Figure 5*). Interestingly, this new contrast suggested the formation of a typical stacked lamellar morphology, usually formed by crystallization in longitudinal flow gradients.

Essentially identical variations in molecular orientation and crystalline morphology were encountered when the same plastic deformation was applied at 100°C, *Figure 10*.

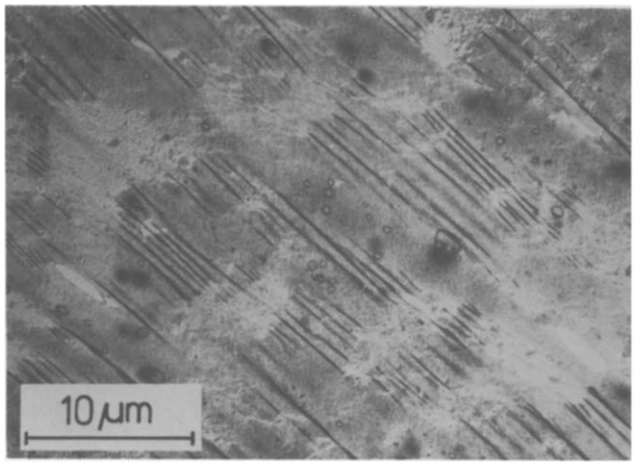

Figure 4 Necking in a thin film of UHMWPE, revealed by reduction of thickness in lighter areas

DISCUSSION

Despite the very simple deformation process, adopted primarily with the aim of following morphological changes directly in the transmission electron microscope, sufficiently high drawing ratios were reached to allow the formation of microfibrils, described in the literature as an alternate sequence of small crystalline and amorphous regions aligned parallel to the drawing direction. Such sequences of new crystalline blocks are clearly revealed under dark field conditions in *Figure 8*, representing the initial stage of microfibril formation. In the absence of necking, on the other hand, original predeformation conditions prevailed in the form of random crystal orientation, *Figure 6a*, and fragmented lamellar contrast, *Figure 7b*. The simple thin film deformation procedure is therefore a convenient choice, when a direct comparison is to be made between a spherulite morphology before and a microfibrillar morphology after the necking process.

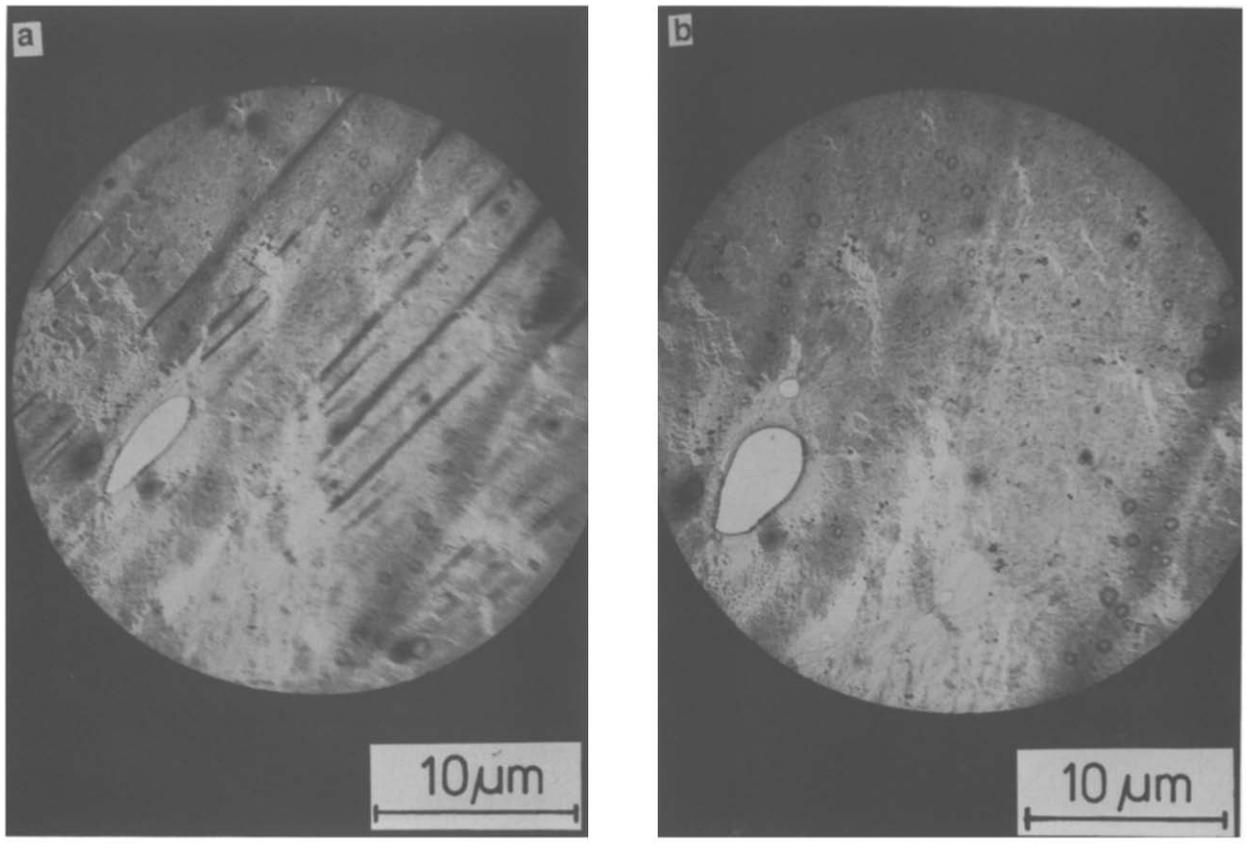

Figure 5 Same area of plastically deformed thin film of UHMWPE, before (a) and after (b) high-intensity electron irradiation in the microscope

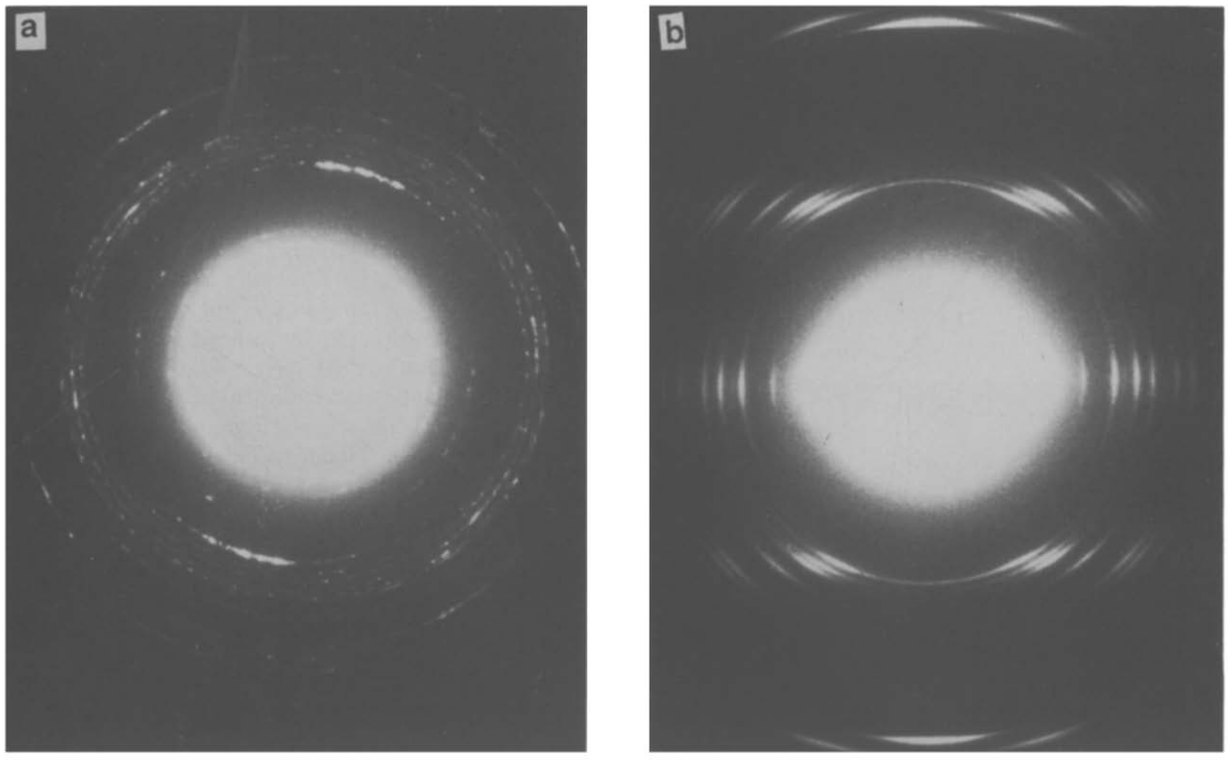

Figure 6 Effect of plastic deformation on crystalline orientation in a thin film of UHMWPE. (a) Less-deformed region; (b) necked area. Compare with *Figure 4*

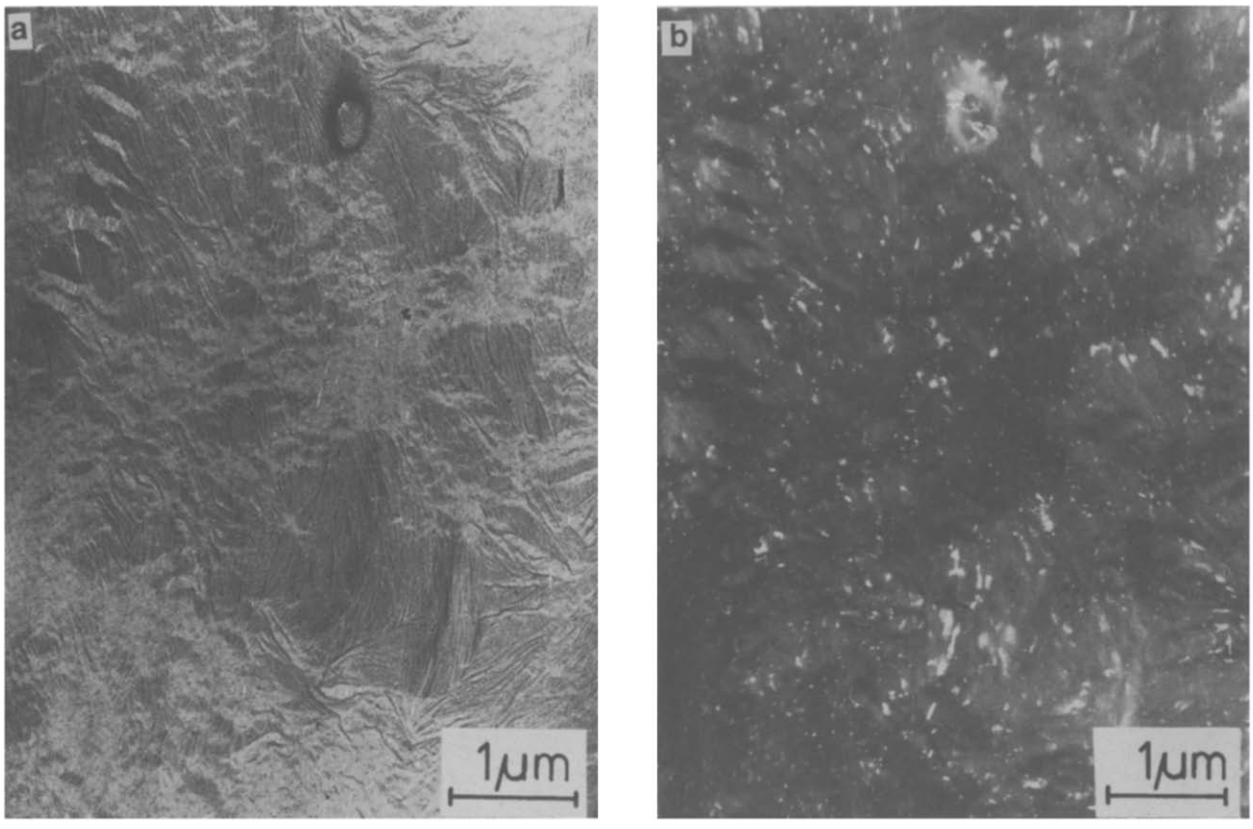

Figure 7 Lamellar destruction and the formation of new, smaller crystal regions due to the plastic deformation of the UHMWPE thin film. (a) Bright field; (b) dark field

The most significant result of the present investigation is believed to be the rather small size of the new crystalline regions which appear at the beginning of microfibril formation. If these regions were simply crystalline fragments of the original lamellae, resulting from some shear or chain slip mechanism as suggested by the model of Peterlin, their longitudinal dimension clearly should remain the same as the original lamellar thickness which was measured to be 20 nm, and not 10 nm as determined for the microfibril crystals.

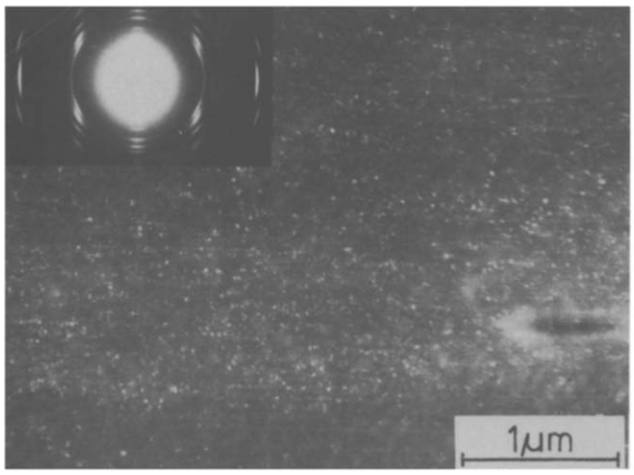

Figure 8 Alignment of new crystals parallel to the drawing direction, as indicated by the electron diffraction pattern shown in the inset. Dark field of the necked region

In principle, two different models could be used in order to explain the formation of 10 nm crystal blocks from 20 nm thick lamellae. Both models have previously been discussed in the literature and are pictured schematically in *Figure 11*. The first alternative, indicated by transition (a) to (b), would simply be the result of local melting. Local melting induced by plastic deformation has in fact been admitted by several authors[10–14], although calculations of the heat generated by the deformation have shown that the temperature rise, even in bulk materials, would not be sufficient to reach melting conditions. On the other hand, the much more rapid dissipation of heat in thin films would suggest that, in the present case, deformation occurred under essentially isothermal conditions.

A more realistic model, which would also explain the smaller size of the new crystal blocks, has been indicated by the sequence (c), (d), (e) in *Figure 11*. In this case, the principal mechanism would be the reorganization under stress of macromolecules which not only are aligned but also partly extended. For this, the chain extension before the recrystallization process could simply occur in the initially amorphous phase, or as the result of complete destruction of the crystalline phase, which would include not only shear or chain slip but also the pull-out of entire chains[7,8,15,16]. Such a complete loss of crystallinity of sheared crystal blocks, termed decrystallization, has actually been observed as the result of plastic deformation[6,16].

A rather surprising observation was the apparent transformation, under electron irradiation, to a typical oriented stacked lamellar morphology, *Figure 9b*. Such

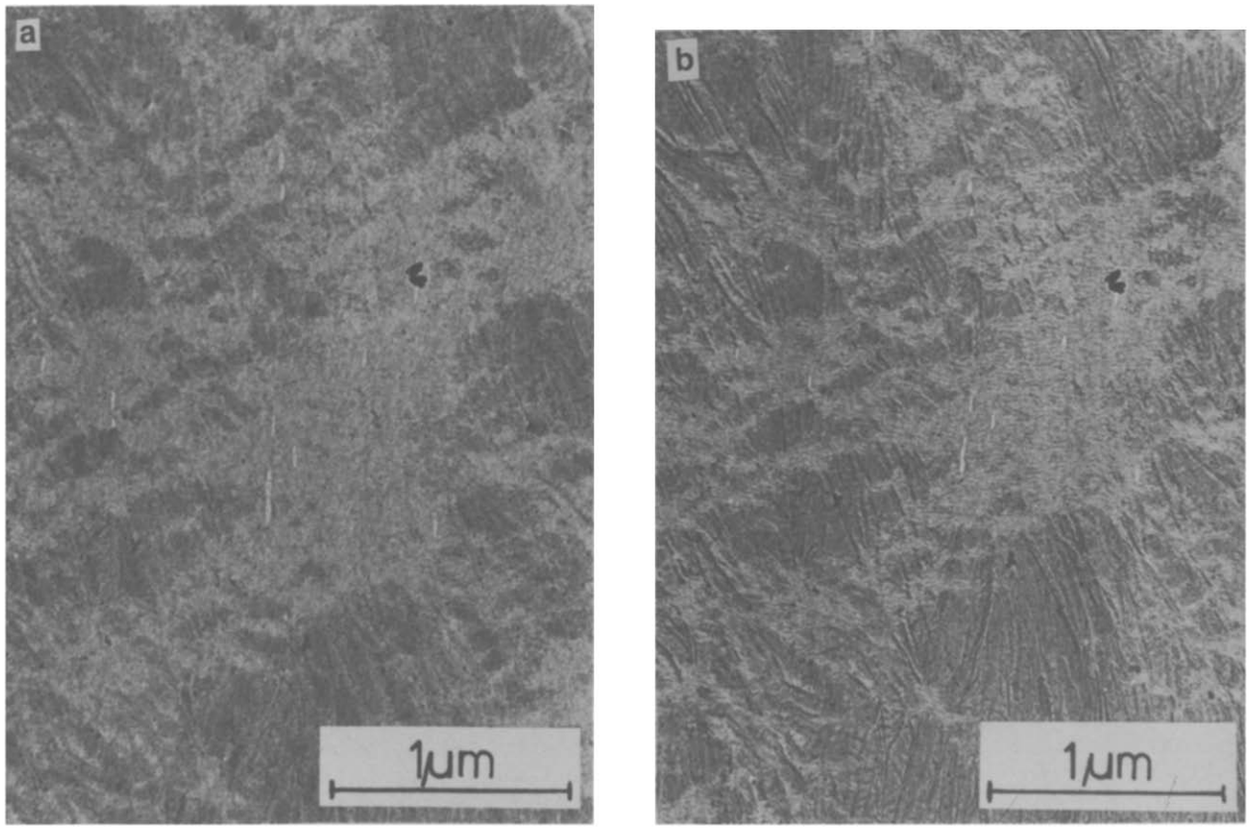

Figure 9 Relaxation of macromolecules after plastic deformation and exposure to the electron beam. Same necked region was photographed before (a) and after (b) high-intensity electron irradiation

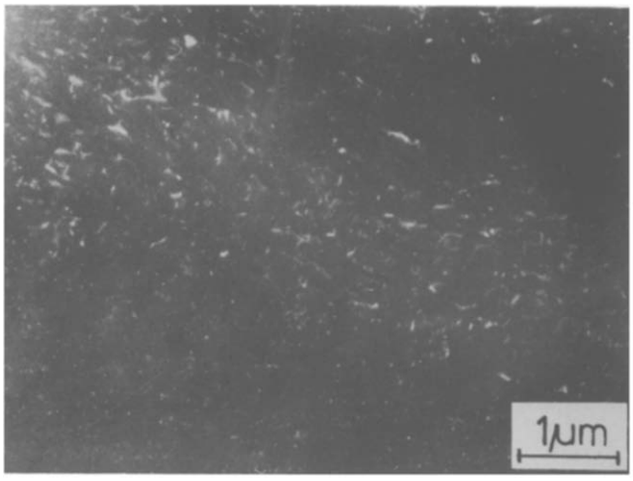

Figure 10 Crystal morphology in a thin film of UHMWPE after deformation at 100°C, dark field

transformation must have been the result of relaxation, similar to what has been observed for the case of recrystallization treatments after plastic deformation of LLDPE[17]. The surprising fact in this case would be the occurrence of radiation-induced crystallization. This should only have been possible due to a rapid rise in temperature of the film in the electron microscope, terminated before the usual radiation damage could lead to the destruction of the crystalline phase.

CONCLUSIONS

Transformations which occur in the crystalline phase of UHMWPE with an initially spherulitic morphology have been investigated by transmission electron microscopy. From the experimental results, the following conclusions have been drawn:

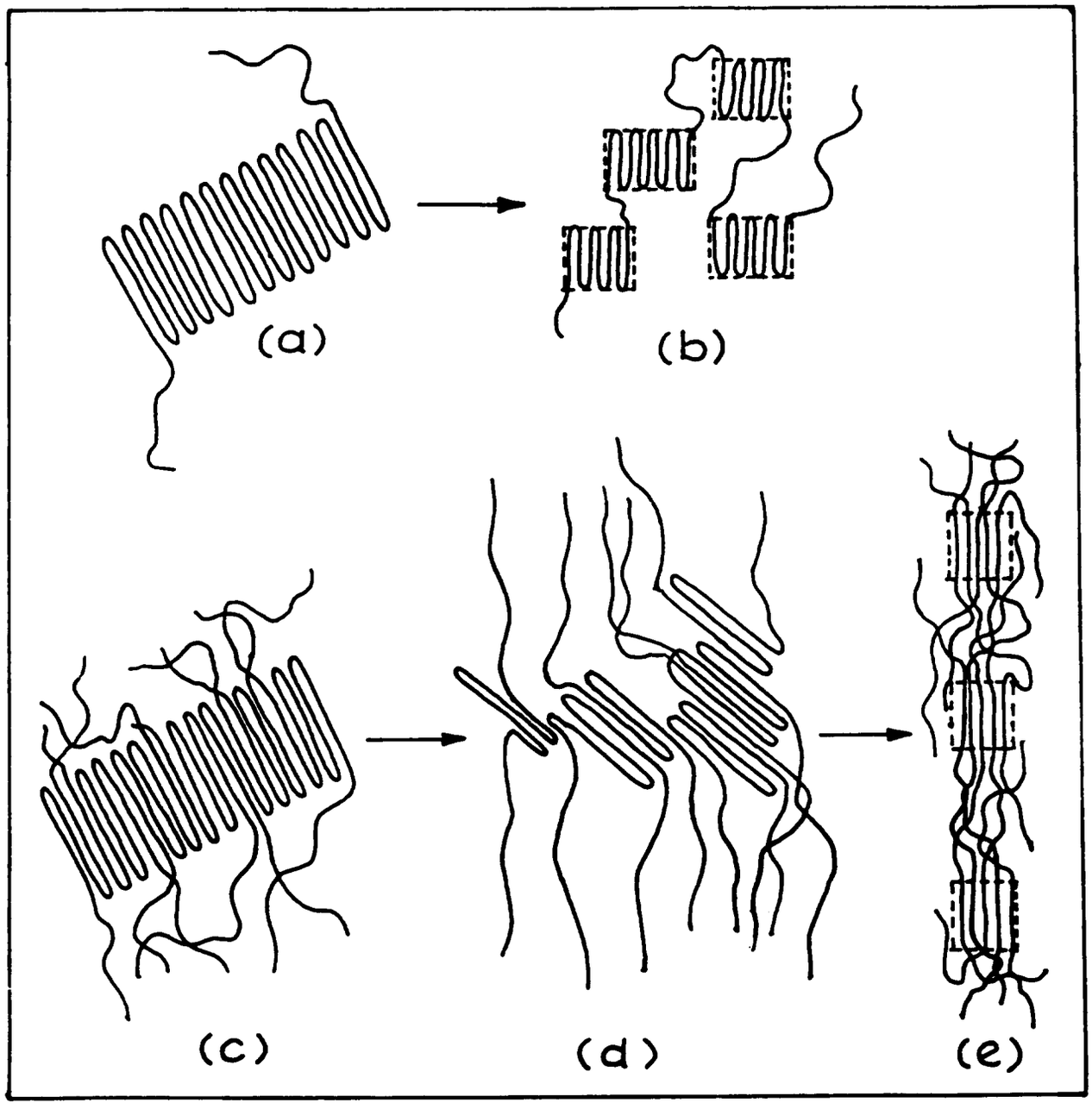

Figure 11 Formation of new crystals of smaller thickness as a result of plastic deformation. From (a) to (b), refolding of macromolecular chains which could occur through recrystallization after localized melting. Sequence (c), (d) and (e) shows the decrystallization of lamellae by shear and chain pull-out, followed by recrystallization and alignment under stress of extended chain segments

- Plastic deformation of thin films in the deformation holder of the electron microscope was found to be an adequate method to study changes in crystalline morphology associated with the necking phenomenon.
- During necking, lamellar structures were destroyed and new oriented crystals were formed which exhibited a smaller size and tended to align themselves parallel to the drawing direction. This process was identified as the initial stage of microfibril formation.
- Arguments were presented in support of a process of recrystallization under stress as the principal mechanism for the formation of the new, deformation-induced microfibrillar morphology.

ACKNOWLEDGEMENTS

H.-J.K. thanks FAPESP, Proc. No. 91/0114-5, for a Visiting Professor's scholarship, and UFSC ar/DEMa for granting a one-year leave of absence. The financial support of the Fonds der Chemischen Industrie (FCI) is also gratefully acknowledged.

REFERENCES

1 DYNEEM, a development project presented by DSM, Marketing Center Chemicals and Polymers, St. Antoniusplein, 6129 EV Urmond, The Netherlands, 1991
2 Kramer, E. J. *J. Appl. Phys.* 1970, **41**, 4327
3 Wada, Y. and Nakayama, A. *J. Appl. Polym. Sci.* 1971, **15**, 183
4 Peterlin, A. *J. Mater. Sci.* 1971, **6**, 490
5 Keller, A. *Proc. R. Soc., Faraday Disc.* 1979, **68**, 145
6 Adams, W. W., Yang, D. and Thomas, E. L. *J. Mater. Sci.* 1986, **21**, 2239
7 Kobayashi, K., cited in Geil, P. H. 'Polymer Single Crystals', Wiley Interscience, New York, 1964, p. 465
8 Petermann, J., Kluge, W. and Gleiter, H. J. *J. Polym. Sci., Polym. Phys. Edn* 1979, **17**, 1043
9 Yoshida, T., Fujiwara, Y. and Asano, T. *Polymer* 1983, **24**, 925
10 Michler, G. H. *Colloid Polym. Sci.* 1992, **270**, 627
11 Juska, T. and Harrison, I. R. *Polym. Eng. Rev.* 1982, **2**, 13
12 Strella, S. J. *Polym. Sci. A-2* 1968, **4**, 527
13 Swallowe, G. M., Field, J. E. and Horn, L. A. *J. Mater. Sci.* 1986, **21**, 4089
14 Philips, P. J. and Philpot, R. J. *Polym. Commun.* 1986, **27**, 307
15 Brady, J. M. and Thomas, E. L. *J. Mater. Sci.* 1989, **24**, 3311
16 Krug, H., Karbach, A. and Petermann, J. *Polymer* 1984, **25**, 1687
17 Furua, M. and Kojama, K. *J. Macromol. Sci.-Phys. (B)* 1986, **25**, 349